

Chapter 2

Many-body systems

We are now ready to generalize the techniques discussed in the previous chapter to systems of interacting particles. We first need to settle on a convenient notation, that will simplify things as much as possible. This is the so-called 2nd quantization, which we briefly discuss next. (It should be familiar to all of you from Phys502).

2.1 Why we need 2nd quantization

As we have seen, we can formulate the quantum mechanics for a single particle in an abstract Hilbert space, although in practice we (almost) always end up working in some given representation, in terms of wavefunctions. Can we generalize this approach to many-body systems? Yes, we can quite easily, if the number N of particles is fixed. In this case, the many-body state in the \vec{r} -representation is (we use again $x = (\vec{r}, \sigma)$):

$$\langle x_1, \dots, x_N | \Psi(t) \rangle = \Psi(x_1, \dots, x_N, t)$$

which is the amplitude of probability that at time t , particle 1 is at $x_1 = (\vec{r}_1, \sigma_1)$, etc. Note that if the number of particles is not fixed (for instance, in a grand-canonical ensemble) we're in some trouble deciding what $\langle |$ to use. But let us ignore this for the moment, and see how we get in trouble even if the number of particles is fixed.

We almost always decompose wavefunctions in a given basis. For a single particle, we know that any wavefunction $\Psi(x, t)$ can be decomposed in terms of a complete and orthonormal basis $\phi_\alpha(x) = \langle x | \alpha \rangle$ as $\Psi(x, t) = \sum_\alpha c_\alpha(t) \phi_\alpha(x)$ – this reduces the problem to that of working with the time-dependent complex numbers $c_\alpha(t)$.

If we have a complete basis for a single-particle Hilbert space, we can immediately generate a complete basis for the N -particle Hilbert space (since the particles are identical), as the products of one-particle basis states:

$$\Psi(x_1, \dots, x_N, t) = \sum_{\alpha_1, \dots, \alpha_N} c_{\alpha_1, \dots, \alpha_N}(t) \phi_{\alpha_1}(x_1) \phi_{\alpha_2}(x_2) \cdots \phi_{\alpha_N}(x_N)$$

However, since the particles are identical, we know that the wavefunctions must be symmetric (for bosons) or antisymmetric (for fermions) to interchange of any particles:

$$\Psi(x_1, \dots, x_N, t) = \xi^P \Psi(x_{P_1}, \dots, x_{P_N}, t)$$

where

$$\begin{pmatrix} 1 & 2 & \dots & N \\ P_1 & P_2 & \dots & P_N \end{pmatrix}$$

is any permutation, P is its sign (number of transpositions), and from now on we use the notation:

$$\xi = \begin{cases} -1, & \text{for fermions} \\ +1, & \text{for bosons} \end{cases} \quad (2.1)$$

It follows immediately that $c_{\dots, \alpha_i, \dots, \alpha_j, \dots} = \xi c_{\dots, \alpha_j, \dots, \alpha_i, \dots}$ and therefore $c_{\dots, \alpha_i, \dots, \alpha_i, \dots} = 0$ for fermions: we cannot have two or more fermions occupying identical states σ_i (the Pauli principle).

Because of this requirement, the physically meaningful many-body fermionic (bosonic) wavefunctions are from the antisymmetric (symmetric) sector of the N -particle Hilbert space, and we only need to keep the properly symmetrized basis states, which we denote as:

$$\phi_{\alpha_1, \dots, \alpha_N}(x_1, \dots, x_N) = \frac{1}{\sqrt{N! \prod_i n_i!}} \sum_{P \in S_N} \xi^P \phi_{\alpha_1}(x_{P_1}) \phi_{\alpha_2}(x_{P_2}) \cdots \phi_{\alpha_N}(x_{P_N}) \quad (2.2)$$

The factor in front is just a normalization constant; n_i is the total number of particles in the same state α_i (only important for bosonic systems), and the summation is over all possible permutations, of which there are $N! / \prod_i n_i!$ distinct ones.

Then, any many-body wavefunction can be written as:

$$\Psi(x_1, \dots, x_N, t) = \sum_{\alpha_1, \dots, \alpha_N} c_{\alpha_1, \dots, \alpha_N}(t) \phi_{\alpha_1, \dots, \alpha_N}(x_1, \dots, x_N)$$

This means that even if we are extremely lucky, and only a single combination of states $\alpha_1, \dots, \alpha_N$ is occupied, so that the sum contains a single $\phi_{\alpha_1, \dots, \alpha_N}(x_1, \dots, x_N)$ basis wavefunction, this alone contains on the order of $N!$ terms (from Eq. (2.2)). If there are more basis states involved in the decomposition of Ψ , then there are that many more terms on the right-hand side of the decomposition.

So now, we can basically see where the inconvenience of working with this approach is. Even if the number of particles is fixed (which is usually not the case); and even if we have managed to solve somehow the problem and find the many-body wavefunction $\Psi(x_1, \dots, x_N, t)$ (which is to say, we know its decomposition coefficients $c_{\alpha_1, \dots, \alpha_N}(t)$ for the given basis) – what we really need in the end are expectation values of single particle operators (such as the total momentum, or particle density, or whatever interests us) or two-particle operators (such as a Coulomb potential interaction). Any single particle operator is of general form $\vec{A} = \sum_{i=1}^N \vec{A}_i$, where \vec{A}_i is the operator acting in the single-particle Hilbert space of particle i . Similarly, two-particle operators are of general form $\vec{B} = \sum_{i < j} \vec{B}_{ij}$, with a total of $N(N-1)/2$ terms. So what we typically have to calculate is something of the form:

$$\langle \Psi | \mathcal{O} | \Psi \rangle = \sum dx_1 \dots \sum dx_N \Psi^*(x_1, \dots, x_N, t) \mathcal{O} \Psi(x_1, \dots, x_N, t)$$

so that we have to perform N integrals over real space (all operators we deal with are diagonal in positions); in general $2N$ sums over spin indexes (which reduce to N if the operator is diagonal in spin-space, as I assumed here) ... and this is out of a combination of a product of order $(N!)^2$ terms contained in $\Psi\Psi^*$, times N or $N(N-1)/2$ terms of the operator. Not impossible, but exceedingly ugly and inelegant to keep track of all these terms. And as I said, if the number of particles is not fixed (for instance, if we work at finite temperature in a system with phonons, where their number will fluctuate) things become that much uglier.

The origin of these complications is the fact that we insisted to work in the \vec{r} -representation, which contains a lot of useless information (which particle is where). In fact, since the particles are identical, all we need to know is what one-particle states are occupied, and we do not need to bother listing which particle is in which state. This is precisely what 2nd quantization does.

2.2 2nd quantization

Notation: from now on, I will use a single index α to label states in a complete single-particle basis (including the spin). For instance, for translationally invariant problems, we will use $\alpha = (\vec{k}, \sigma)$ as quantum numbers, whereas if we have SHO, we can use $\alpha = (n, \sigma)$, etc. α is simply the ensemble of quantum numbers needed to characterize the single-particle state.

Moreover, we define an ordering for the states α , for instance, we order them in increasing order of energy for some single-particle Hamiltonian $E_1 < E_2 < \dots$ so that state “1” (quantum numbers α_1) has the lowest energy, state “2” (quantum numbers α_2) has the next highest energy, etc. If there are degenerate states, we define some rule to order the states, e.g. spin-up first and spin-down second.

Once this ordering is agreed upon, we define the abstract vectors:

$$|n_1, n_2, \dots\rangle \quad (2.3)$$

as being the state with n_1 particles in state “1”, n_2 particles in state “2”, etc. We have to list occupation numbers for all possible states – for an empty state, $n_i = 0$. Of course, for fermionic systems we can only have $n_i = 0$ or 1, for any state (Pauli’s principle). For bosons, n_i can be any non-negative integer.

Examples: the ground-state for non-interacting fermions will be represented as $|1, 1, \dots, 1, 0, 0, \dots\rangle$ (first lowest-energy N states are occupied) whereas the ground-state of a non-interacting bosonic system is $|N, 0, 0, \dots\rangle$ (all bosons in the lowest energy state).

The ensemble of all possible states $\{|n_1, n_2, \dots\rangle\}$ is a complete orthonormal basis, of the so-called Fock space. This contains the Hilbert (fermionic or bosonic) subspaces for any number of particles, from zero (the vacuum is simply $|0\rangle = |0, 0, \dots\rangle$ i.e. no particle in any states) to any desired number N . If the number of particles is fixed, we work in the subspace of the Fock space defined by the constrain $N = \sum_i n_i$.

We would like now to be able to generate easily these states, and also be able to work with operators represented directly in this Fock space, so that computing matrix elements is straightforward. Remember that these are identical particles, so these basis states must obey the proper statistics. We enforce this in the following way: to each state α we associate a pair of operators $c_\alpha, c_\alpha^\dagger$ which obey the algebra:

$$\begin{aligned} c_\alpha c_\beta^\dagger - \xi c_\beta^\dagger c_\alpha &= [c_\alpha, c_\beta^\dagger]_\xi = \delta_{\alpha, \beta} \\ [c_\alpha, c_\beta]_\xi &= [c_\alpha^\dagger, c_\beta^\dagger]_\xi = 0 \end{aligned} \quad (2.4)$$

We use the notation $[a, b]_\xi = ab - \xi ba$ to deal simultaneously with both fermions ($\xi = -1$) and bosons ($\xi = 1$). When dealing with a well-defined type, we will use the usual notation for commutators $[,]_+ = [,]$ and for anticommutators $[,]_- = \{, \}$. Also, usually we call fermionic operators as $a_\alpha, a_\alpha^\dagger$, and bosonic operators $b_\alpha, b_\alpha^\dagger$. I will use the c operators when I want to deal with both types simultaneously.

For fermions, the Pauli’s principle is obeyed, since the second line of the Wigner-Pauli algebra gives that: $(a_\alpha^\dagger)^2 = (a_\alpha)^2 = 0$: we can’t create or annihilate two fermions in/from the same state.

Let $\hat{n}_\alpha = a_\alpha^\dagger a_\alpha$. Then, for fermions we see right away that $\hat{n}_\alpha \hat{n}_\alpha = a_\alpha^\dagger a_\alpha a_\alpha^\dagger a_\alpha = a_\alpha^\dagger (1 - a_\alpha^\dagger a_\alpha) a_\alpha = \hat{n}_\alpha$. In other words, the operator \hat{n}_α can only have eigenvalues 0 or 1. Let us look at each α individually (and not write the label, for the moment). Starting from $\hat{n}|0\rangle = 0; \hat{n}|1\rangle = |1\rangle$ and the anticommutation relations, one can show that:

$$\begin{aligned} a^\dagger|0\rangle &= |1\rangle & a|0\rangle &= 0 \\ a^\dagger|1\rangle &= 0 & a|1\rangle &= |0\rangle \end{aligned}$$

so that we can write

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

for the state with n particles in state α .

Similarly, for bosons we have that if $\hat{n}|n\rangle = n|n\rangle$ is an eigenstate of the number operator, then $n = \langle n|b^\dagger b|n\rangle \geq 0$. Using the commutation relations, one can show that $\hat{n}(b|n\rangle) = (n-1)(b|n\rangle)$ and $\hat{n}(b^\dagger|n\rangle) = (n+1)(b^\dagger|n\rangle)$, i.e. b and b^\dagger are raising and lowering operators. This leads to the conclusion that the eigenvalues n must be non-negative integers, and the proper normalization is found to be:

$$\begin{aligned} b^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\ b|n\rangle &= \sqrt{n}|n-1\rangle \end{aligned}$$

and again, one can express the state with n bosons in state α as:

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

for any $n = 0, 1, 2, \dots$ (Note: all these things should be well-known to you. I am trying here to remind you how they were derived, but if you are not familiar with this, you should read first part of first chapter in Negele and Orland, where these things are introduced properly).

Definition: we define the general Fock state as:

$$|n_1, n_2, \dots\rangle = \frac{(c_1^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(c_2^\dagger)^{n_2}}{\sqrt{n_2!}} \dots |0\rangle \quad (2.5)$$

where $|0\rangle = |0, 0, \dots\rangle$ is the vacuum.

Note: for fermions, since the operators anticommute, the order in which we write the operators is very important!

The actions of the operators on a Fock state can now be found just by following these rules. Let me show one example in detail:

$$c_\alpha|\dots, n_\alpha, \dots\rangle = c_\alpha \frac{(c_1^\dagger)^{n_1}}{\sqrt{n_1!}} \dots \frac{(c_\alpha^\dagger)^{n_\alpha}}{\sqrt{n_\alpha!}} \dots |0\rangle$$

C_α (anti)commutes with all operators before arriving near $(c_\alpha^\dagger)^{n_\alpha}$. There are $n_1 + \dots n_{\alpha-1}$ such operators. We define the numbers::

$$S_\alpha = \sum_{i=1}^{\alpha-1} n_i$$

and so:

$$c_\alpha \frac{(c_1^\dagger)^{n_1}}{\sqrt{n_1!}} \dots \frac{(c_\alpha^\dagger)^{n_\alpha}}{\sqrt{n_\alpha!}} \dots |0\rangle = \xi^{S_\alpha} \frac{(c_1^\dagger)^{n_1}}{\sqrt{n_1!}} \dots c_\alpha \frac{(c_\alpha^\dagger)^{n_\alpha}}{\sqrt{n_\alpha!}} \dots |0\rangle$$

Since (this is true for both fermions and bosons, see above)

$$c_\alpha|n_\alpha\rangle = \sqrt{n_\alpha}|n_\alpha-1\rangle$$

we find immediately that:

$$c_\alpha|n_1, \dots, n_\alpha, \dots\rangle = \xi^{S_\alpha} \sqrt{n_\alpha}|n_1, \dots, n_\alpha-1, \dots\rangle$$

This looks quite similar to what we had above, except for the factor $\xi^{S_\alpha} = \pm 1$ which keeps track of the ordering and how many other states in “front” of state α are occupied. This sign is obviously very important (for fermions; for bosons it is always 1). Similarly, one finds that:

$$c_\alpha^\dagger |n_1, \dots, n_\alpha, \dots\rangle = \xi^{S_\alpha} \sqrt{\xi n_\alpha + 1} |n_1, \dots, n_\alpha + 1, \dots\rangle$$

With these two, we can now compute the action of any operators (since, as we show next, any operator can be written in terms of creation and annihilation operators).

Just one more example, to see that we get sensible results. Applying twice these rules, we find

$$c_\alpha^\dagger c_\alpha |n_1, \dots, n_\alpha, \dots\rangle = \xi^{S_\alpha} \sqrt{n_\alpha} c_\alpha^\dagger |n_1, \dots, n_\alpha - 1, \dots\rangle = \xi^{S_\alpha} \sqrt{n_\alpha} \xi^{S_\alpha} \sqrt{\xi(n_\alpha - 1) + 1} |n_1, \dots, n_\alpha, \dots\rangle$$

Since $\xi^2 = 1 \rightarrow \xi^{2S_\alpha} = 1$. If $\xi = 1 \rightarrow \sqrt{n_\alpha[\xi(n_\alpha - 1) + 1]} = n_\alpha$. If $\xi = -1$, then $\sqrt{n_\alpha[\xi(n_\alpha - 1) + 1]} = \sqrt{n_\alpha(2 - n_\alpha)} = n_\alpha$, since in this case we’re dealing with fermions, and we can only have $n_\alpha = 0, 1$. So we find, as expected, that:

$$\hat{n}_\alpha |n_1, \dots, n_\alpha, \dots\rangle = n_\alpha |n_1, \dots, n_\alpha, \dots\rangle$$

The only other question we need to answer now, is how to write general operators in terms of these creation and annihilation operators? Here’s the answer:

Theorem: If $\hat{A} = \sum_{i=1}^N \mathcal{A}_i$ is a single-particle operator, with \mathcal{A}_i acting only on particle “i”, then:

$$\hat{A} = \sum_{\alpha, \alpha'} \langle \alpha | \mathcal{A} | \alpha' \rangle c_\alpha^\dagger c_{\alpha'} \quad (2.6)$$

where

$$\langle \alpha | \mathcal{A} | \alpha' \rangle = \sum_{\sigma, \sigma'} \int d\vec{r} \phi_\alpha^*(\vec{r}, \sigma) \langle \vec{r}, \sigma | \mathcal{A} | \vec{r}, \sigma' \rangle \phi_{\alpha'}(\vec{r}, \sigma') \quad (2.7)$$

I will not reproduce the proof (look in a textbook), but let me try to justify this. First, since a single-particle operator acts on just one particle (can be any of them), all it can do is either to leave it in the state it was in, $\alpha \rightarrow \alpha$, or change its state $\alpha' \rightarrow \alpha$. All terms in Eq. (2.6) describe such processes. The question is how to find the coefficients for each process, namely $\langle \alpha | \mathcal{A} | \alpha' \rangle$. This is done so that the matrix elements of \hat{A} in a complete basis are correct – it is a straightforward, but boring and time-consuming task to verify that Eq. (2.7) is the correct answer. Note: in writing Eq. (2.7), I assumed that the single-particle operator \mathcal{A} is diagonal in position, which is basically always the case. I’ll show some examples in a bit, but before that let me state the result for two-particle operators:

Theorem: If $\hat{B} = \frac{1}{2} \sum_{i \neq j} \mathcal{B}_{i,j}$ is a two-particle operator, with $\mathcal{B}_{i,j}$ acting only on particles “i” and “j” ($1 \leq i, j \leq N$), then:

$$\hat{B} = \frac{1}{2} \sum_{\substack{\alpha, \alpha' \\ \beta, \beta'}} \langle \alpha, \beta | \mathcal{B} | \alpha', \beta' \rangle c_\alpha^\dagger c_\beta^\dagger c_{\beta'} c_{\alpha'} \quad (2.8)$$

where

$$\langle \alpha, \beta | \mathcal{B} | \alpha', \beta' \rangle = \sum_{\substack{\sigma_1, \sigma'_1 \\ \sigma_2, \sigma'_2}} \int d\vec{r}_1 \int d\vec{r}_2 \phi_\alpha^*(\vec{r}_1, \sigma_1) \phi_\beta^*(\vec{r}_2, \sigma_2) \langle \vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2 | \mathcal{B} | \vec{r}_1, \sigma'_1; \vec{r}_2, \sigma'_2 \rangle \phi_{\alpha'}(\vec{r}_1, \sigma'_1) \phi_{\beta'}(\vec{r}_2, \sigma'_2) \quad (2.9)$$

NOTE the order of listing the annihilation operators in Eq. (2.8) !!! Do not list them in the “expected” order $c_{\alpha'}c_{\beta'}$, since for fermions that implies changing the sign of the interaction from attractive to repulsive (or vice-versa) and that’s bound to make all the subsequent results wrong!

All I’m going to say about two-particle operators, is that since they act on two particles, they can change the states of the two particles (or not), and that’s precisely what all terms in Eq. (2.8) describe.

Let’s see some examples, before you start thinking that this is all too complicated. We start first with some single-particle operators:

(a) The kinetic energy $\hat{T} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m}$. Since

$$\langle \vec{r}, \sigma | \frac{\hat{p}^2}{2m} | \vec{r}, \sigma' \rangle = \delta_{\sigma, \sigma'} \left(\frac{-\hbar^2}{2m} \nabla^2 \right)$$

(the well-known \vec{r} -representation of the kinetic energy of a single particle), we find:

$$\hat{T} = \sum_{\alpha, \alpha'} \langle \alpha | \frac{\hat{p}^2}{2m} | \alpha' \rangle c_{\alpha}^{\dagger} c_{\alpha'}$$

where

$$\langle \alpha | \frac{\hat{p}^2}{2m} | \alpha' \rangle = \sum_{\sigma} \int d\vec{r} \phi_{\alpha}^*(\vec{r}, \sigma) \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \phi_{\alpha'}(\vec{r}, \sigma)$$

Let’s go a bit farther, and assume that the basis $\alpha = (\vec{k}, \sigma)$ are the eigenstates of the momentum operator, so that $\phi_{\vec{k}, \sigma}(\vec{r}, \sigma) = \delta_{\sigma, \sigma'} \exp(i\vec{k} \cdot \vec{r}) / \sqrt{V}$ are just plane-waves. Then

$$\langle \vec{k}, \sigma | \frac{\hat{p}^2}{2m} | \vec{k}', \sigma' \rangle = \delta_{\sigma, \sigma'} \delta_{\vec{k}, \vec{k}'} \frac{\hbar^2 \vec{k}^2}{2m}$$

(which you can either write down directly, or check by doing the integral I wrote above, for these particular basis states), and so, in this basis:

$$\hat{T} = \sum_{\vec{k}, \sigma} \frac{\hbar^2 \vec{k}^2}{2m} c_{\vec{k}, \sigma}^{\dagger} c_{\vec{k}, \sigma} \quad (2.10)$$

which, you should agree, makes a lot of sense. What this tells us is that this operator counts how many particles have a given momentum \vec{k} and spin σ (i.e., $\hat{n}_{\vec{k}, \sigma} = c_{\vec{k}, \sigma}^{\dagger} c_{\vec{k}, \sigma}$), multiplies by the kinetic energy associated with this state $\frac{\hbar^2 \vec{k}^2}{2m}$, and sums over all possible states. You should show now that the number of particles operator $\hat{N} = \sum_{i=1}^N 1 \rightarrow \sum_{\alpha} c_{\alpha}^{\dagger} c_{\alpha}$, no matter what basis we use.

Note: the operator in the second-quantized form is independent of the number of particles N ! In the first quantization, if I have a wavefunction with N particles, then the kinetic energy must be the sum of the N single-particle kinetic energies. If I have $N + 2$ particles, then the kinetic energy is a different operator, with $N + 2$ terms. On the other hand, in the second-quantization, the kinetic energy always is like in Eq. (2.10) (if we choose this basis). This means we can act with it on wavefunctions which are superpositions of states with different numbers of particles, with no problem! This is a significant improvement.

I will show one more example, and give as assignment a few more usually encountered single-particle operators, so that you see that the final result is always what common-sense would predict.

(b) Total spin operator, $\vec{S} = \sum_{i=1}^N \vec{s}_i$. For simplicity, let us assume we're still in the basis $\alpha = (\vec{k}, \sigma)$. We need the matrix elements, let's compute them for each spin projection alone. I will assume that we work with spins 1/2, which can be written in terms of the Pauli matrices $\vec{s} = \frac{\hbar}{2}\vec{\sigma}$. Then:

$$\langle \vec{k}, \sigma | s_z | \vec{k}', \sigma' \rangle = \frac{\hbar}{2} \delta_{\vec{k}, \vec{k}'} \delta_{\sigma, \sigma'} \sigma$$

so that

$$\hat{S}_z = \frac{\hbar}{2} \sum_{\vec{k}, \sigma} \sigma c_{\vec{k}, \sigma}^\dagger c_{\vec{k}, \sigma} = \frac{\hbar}{2} \sum_{\vec{k}} (c_{\vec{k}\uparrow}^\dagger c_{\vec{k}\uparrow} - c_{\vec{k}\downarrow}^\dagger c_{\vec{k}\downarrow})$$

i.e, simply subtract the number of particles with spin down from those with spin-up, to find the total spin in the z -direction. Similarly:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y = \hbar \sum_{\vec{k}} c_{\vec{k}\uparrow}^\dagger c_{\vec{k}\downarrow}$$

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y = \hbar \sum_{\vec{k}} c_{\vec{k}\downarrow}^\dagger c_{\vec{k}\uparrow}$$

simply raise or lower the total spin, by flipping spins-down into spins-up, or viceversa. Putting all together, we can write:

$$\vec{S} = \sum_{\vec{k}, \sigma, \sigma'} c_{\vec{k}, \sigma}^\dagger \frac{\hbar \vec{\sigma}_{\sigma\sigma'}}{2} c_{\vec{k}, \sigma'}$$

where $\vec{\sigma}_{\sigma\sigma'}$ are the matrix elements of the Pauli matrices.

(c) Two-particle operator $\hat{V} = \frac{1}{2} \sum_{i \neq j} u(\vec{r}_i - \vec{r}_j)$ for two-particle interactions (for instance, $u(\vec{r}) = e^2/r$ can be Coulomb interactions). For simplicity, I assume that the interactions depend only on the distance between particles, but not on their spins (true for Coulomb).

We'll continue to work in the basis $\alpha = (\vec{k}, \sigma)$, so that the basis wavefunctions are simple planewaves $\langle \vec{r} | \vec{k} \rangle = e^{i\vec{k}\vec{r}}/\sqrt{V}$, where V is the volume of the system. (I will assume V finite to begin with, since in this case the allowed \vec{k} values are discrete, and it makes sense to write $\sum_{\vec{k}}$, not $\int d\vec{k}$. We can let $V \rightarrow \infty$ at the end, if need be.) Since:

$$\langle \vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2 | u(\vec{r} - \vec{r}') | \vec{r}_1, \sigma'_1; \vec{r}_2, \sigma'_2 \rangle = u(\vec{r}_1 - \vec{r}_2) \delta_{\sigma_1, \sigma'_1} \delta_{\sigma_2, \sigma'_2}$$

Eq. (2.9) becomes:

$$\langle \vec{k}_1, \sigma_1; \vec{k}_2, \sigma_2 | u | \vec{k}_3, \sigma_3; \vec{k}_4, \sigma_4 \rangle = \delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4} \int d\vec{r}_1 \int d\vec{r}_2 \frac{e^{-i\vec{k}_1\vec{r}_1 - i\vec{k}_2\vec{r}_2}}{V} u(\vec{r}_1 - \vec{r}_2) \frac{e^{i\vec{k}_3\vec{r}_1 + i\vec{k}_4\vec{r}_2}}{V}$$

We now define the Fourier transform of the interaction potential:

$$u(\vec{r}) = \frac{1}{V} \sum_{\vec{q}} e^{i\vec{q}\vec{r}} u_{\vec{q}}; \quad u_{\vec{q}} = \int d\vec{r} e^{-i\vec{q}\vec{r}} u(\vec{r})$$

Using the identity $\int d\vec{r} e^{i(\vec{k}-\vec{k}')\vec{r}} = V \delta_{\vec{k}, \vec{k}'}$ we can now do the two integrals over \vec{r}_1, \vec{r}_2 easily. The end result, which we will use extensively, is:

$$\hat{V} = \frac{1}{2V} \sum_{\substack{\vec{k}, \vec{k}' \\ \sigma, \sigma'}} \sum_q u_{\vec{q}} c_{\vec{k}+\vec{q}, \sigma}^\dagger c_{\vec{k}'-\vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'} c_{\vec{k}, \sigma} \quad (2.11)$$

In other words, two particles that initially were in the states $(\vec{k}, \sigma), (\vec{k}', \sigma')$ have interacted with one another, exchanged some momentum \vec{q} (but with total momentum conserved, as it should be since this interaction is invariant to global translations), and end up in the states $(\vec{k} + \vec{q}, \sigma), (\vec{k}' - \vec{q}, \sigma')$.

We can similarly write the second-quantization expression for any operator. Since we know how c, c^\dagger act on Fock states $|n_1, \dots\rangle$, we can then easily and efficiently perform calculations.

However, one less-than-ideal feature is that all this notation is dependent on the specific choice for the basis α . It would be very convenient to be able to have some sort of general formulation that is independent of the single-particle basis, so we can write general formulae ... and then when needed, we can go to the basis most appropriate for the problem at hand.

This, of course, can be done (or I would not have mentioned it). We define the *field operators*:

$$\hat{\Psi}(\vec{r}) = \sum_{\alpha} \phi_{\alpha}(\vec{r})c_{\alpha}; \quad \hat{\Psi}^{\dagger}(\vec{r}) = \sum_{\alpha} \phi_{\alpha}^T(\vec{r})c_{\alpha}^{\dagger} \quad (2.12)$$

where (see very first section)

$$\phi_{\alpha}(\vec{r}) = \begin{pmatrix} \phi_{\alpha}(\vec{r}, +S) \\ \dots \\ \phi_{\alpha}(\vec{r}, -S) \end{pmatrix} \text{ and } \phi_{\alpha}^T(\vec{r}) = \left(\phi_{\alpha}^*(\vec{r}, +S), \dots, \phi_{\alpha}^*(\vec{r}, -S) \right)$$

are $2S + 1$ -spinors. Using the completeness of the basis α and the commutation relations $[c_{\alpha}^{\dagger}, c_{\beta}]_{\xi} = \delta_{\alpha, \beta}$ etc., it is straightforward to show that the field operators satisfy the commutation relations:

$$[\hat{\Psi}(\vec{r}), \hat{\Psi}^{\dagger}(\vec{r}')]_{\xi} = \delta(\vec{r} - \vec{r}'); \quad [\hat{\Psi}(\vec{r}), \hat{\Psi}(\vec{r}')]_{\xi} = [\hat{\Psi}^{\dagger}(\vec{r}), \hat{\Psi}^{\dagger}(\vec{r}')]_{\xi} = 0 \quad (2.13)$$

Before going on, let's see what is the meaning of these operators. Consider the action of $\hat{\Psi}^{\dagger}(\vec{r})$ on the vacuum:

$$\hat{\Psi}^{\dagger}(\vec{r})|0\rangle = \sum_{\alpha} \phi_{\alpha}^T(\vec{r})c_{\alpha}^{\dagger}|0\rangle = \sum_{\alpha} \phi_{\alpha}^T(\vec{r})|0, \dots, n_{\alpha} = 1, 0, \dots\rangle$$

I can also write $|0, \dots, n_{\alpha} = 1, 0, \dots\rangle = |\alpha\rangle$, since this is the state with a single particle in state α , and so it follows that:

$$\langle \vec{r}' | \hat{\Psi}^{\dagger}(\vec{r}) | 0 \rangle = \sum_{\alpha} \phi_{\alpha}^T(\vec{r}) \phi_{\alpha}(\vec{r}') = \delta(\vec{r} - \vec{r}')$$

since the basis is complete. It follows that it must be that:

$$\hat{\Psi}^{\dagger}(\vec{r})|0\rangle = |\vec{r}\rangle$$

i.e. this operator creates a particle at position \vec{r} . It can be shown that this is true in any state (not only vacuum). Similarly, it can be shown that the operator $\hat{\Psi}(\vec{r})$ destroys (removes) a particle from position \vec{r} .

Using again the completeness and orthonormality of the basis α , we can invert Eqs. (2.12) to find:

$$c_{\alpha} = \int d\vec{r} \phi_{\alpha}^T(\vec{r}) \hat{\Psi}(\vec{r}); \quad c_{\alpha}^{\dagger} = \int d\vec{r} \hat{\Psi}^{\dagger}(\vec{r}) \phi_{\alpha}(\vec{r}) \quad (2.14)$$

and substituting this in Eqs. (2.6), (2.8) we find the representations:

$$\hat{A} = \sum_{i=1}^N \mathcal{A}_i \rightarrow \int d\vec{r} \hat{\Psi}^{\dagger}(\vec{r}) \mathcal{A}_{\vec{r}} \hat{\Psi}(\vec{r}) \quad (2.15)$$

and

$$\vec{B} = \frac{1}{2} \sum_{i \neq j} \mathcal{B}_{ij} \rightarrow \frac{1}{2} \int d\vec{r} \int d\vec{r}' \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') \mathcal{B}_{\vec{r}, \vec{r}'} \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r}) \quad (2.16)$$

(note the order of operators!!!), where I used the simplified notation $\mathcal{A}_{\vec{r}} = \langle \vec{r}' | \mathcal{A} | \vec{r} \rangle$ – this is a $2S + 1 \times 2S + 1$ matrix, because of the spin – and similarly for B (which is a direct product of two $2S + 1 \times 2S + 1$ matrices). (Don't worry, we'll soon introduce friendlier notation, so we won't need to deal with these matrices. But let's be formal just for a bit more.)

It follows that:

(a) $\hat{T} = \int d\vec{r} \hat{\Psi}^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \hat{\Psi}(\vec{r});$

(b) density operator $\vec{n}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \rightarrow \int d\vec{r}' \hat{\Psi}^\dagger(\vec{r}') \delta(\vec{r} - \vec{r}') \hat{\Psi}(\vec{r}') = \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r})$

(c) total number of particles $\vec{N} = \sum_{i=1}^N 1 \rightarrow \int d\vec{r} \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}) = \int d\vec{r} \vec{n}(\vec{r})$

(d) Coulomb interaction: $\hat{V} = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') u(\vec{r} - \vec{r}') \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r})$

etc. In particular, the Hamiltonian for particles in an external field and also interacting with one another:

$$\mathcal{H} = \int d\vec{r} \hat{\Psi}^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + u_{ext}(\vec{r}) \right) \hat{\Psi}(\vec{r}) + \frac{1}{2} \int d\vec{r} \int d\vec{r}' \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') u(\vec{r} - \vec{r}') \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r}) \quad (2.17)$$

looks very appealing, and is again independent on the number of particles that may be in the system (or whether it is constant or not). As I said, this makes it very easy to work with states in which the number of particles is not fixed, such as is the case in grand-canonical ensembles, for instance.

When we discuss Green's functions (2 sections from now) we will derive the equation of motion for the field operator $\hat{\Psi}(\vec{r})$ and see that it is very similar in form to Schrödinger's equation. In the absence of particle-particle interactions, as we will see, we have $i\hbar \frac{d}{dt} \hat{\Psi}(\vec{r}, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + u_{ext}(\vec{r}) \right) \hat{\Psi}(\vec{r}, t)$. Interactions add a second term, which we will discuss at the appropriate time. The reason I'm mentioning this now, is that it gives you a sense of why this is called the second quantization. In the first quantization (going from classical to quantum mechanics) we quantize the operators, and use a wavefunction $\phi(\vec{r})$ to characterize the state of the system. This wavefunction $\phi(\vec{r})$ can be regarded as a "classical field" of its own. In the second quantization, it is as if we now also quantize the wavefunction into the field operator $\hat{\Psi}(\vec{r})$.

Now, let us simplify the notation and remove the need of working with matrices if the spin $S > 0$. In all cases we can choose the basis $\alpha = (\tilde{\alpha}, \sigma)$, i.e. one of the quantum numbers is the spin, and then $\tilde{\alpha}$ contains all other quantum numbers needed to describe the translational sector of the Hilbert space (e.g., the momentum of the particle).

We can then define various *spin-components of the field operators*:

$$\hat{\Psi}_\sigma(\vec{r}) = \sum_{\tilde{\alpha}} \phi_{\tilde{\alpha}}(\vec{r}) c_{\tilde{\alpha}, \sigma}; \quad \hat{\Psi}_\sigma^\dagger(\vec{r}) = \sum_{\tilde{\alpha}} \phi_{\tilde{\alpha}}^*(\vec{r}) c_{\tilde{\alpha}, \sigma}^\dagger \quad (2.18)$$

If $\tilde{\alpha} = \vec{k}$, then $\phi_{\tilde{\alpha}}(\vec{r}) \rightarrow e^{i\vec{r}\vec{k}} / \sqrt{V}$ and is a simple number, not a $2S + 1$ -dim spinor. So the spin-components $\hat{\Psi}_\sigma(\vec{r})$, $\hat{\Psi}_\sigma^\dagger(\vec{r})$ are simple operators, not matrices of operators. Their meaning is that they annihilate or create a particle *with spin* σ at position \vec{r} .

It is now straightforward to verify (by repeating previous calculations) that:

$$[\hat{\Psi}_\sigma(\vec{r}), \hat{\Psi}_{\sigma'}^\dagger(\vec{r}')]_\xi = \delta_{\sigma, \sigma'} \delta(\vec{r} - \vec{r}'); \quad [\hat{\Psi}_\sigma(\vec{r}), \hat{\Psi}_{\sigma'}(\vec{r}')]_\xi = [\hat{\Psi}_\sigma^\dagger(\vec{r}), \hat{\Psi}_{\sigma'}^\dagger(\vec{r}')]_\xi = 0 \quad (2.19)$$

and to show that:

$$\hat{A} = \sum_{i=1}^N \mathcal{A}_i \rightarrow \sum_{\sigma, \sigma'} \int d\vec{r} \hat{\Psi}_\sigma^\dagger(\vec{r}) \langle \sigma | \mathcal{A}_{\vec{r}} | \sigma' \rangle \hat{\Psi}_{\sigma'}(\vec{r}) \quad (2.20)$$

and

$$\vec{B} = \frac{1}{2} \sum_{i \neq j} \mathcal{B}_{ij} \rightarrow \frac{1}{2} \sum_{\substack{\sigma_1, \sigma_2 \\ \sigma_3, \sigma_4}} \int d\vec{r} \int d\vec{r}' \hat{\Psi}_{\sigma_1}^\dagger(\vec{r}) \hat{\Psi}_{\sigma_2}^\dagger(\vec{r}') \langle \sigma_1, \sigma_2 | \mathcal{B}_{\vec{r}, \vec{r}'} | \sigma_3, \sigma_4 \rangle \hat{\Psi}_{\sigma_4}(\vec{r}') \hat{\Psi}_{\sigma_3}(\vec{r}) \quad (2.21)$$

where $\langle \sigma | \mathcal{A}_{\vec{r}} | \sigma' \rangle = \langle \vec{r}, \sigma | \mathcal{A} | \vec{r}, \sigma' \rangle$ and $\langle \sigma_1, \sigma_2 | \mathcal{B}_{\vec{r}, \vec{r}'} | \sigma_3, \sigma_4 \rangle = \langle \vec{r}, \sigma_1; \vec{r}', \sigma_2 | \mathcal{B} | \vec{r}, \sigma_3; \vec{r}', \sigma_4 \rangle$. In particular, if the operators are spin independent, then these matrix elements are proportional to $\delta_{\sigma, \sigma'}$, respectively $\delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4}$. As a result, a typical Hamiltonian becomes:

$$\mathcal{H} = \sum_{\sigma} \int d\vec{r} \hat{\Psi}_{\sigma}^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + u_{ext}(\vec{r}) \right) \hat{\Psi}_{\sigma}(\vec{r}) + \frac{1}{2} \sum_{\sigma, \sigma'} \int d\vec{r} \int d\vec{r}' \hat{\Psi}_{\sigma}^\dagger(\vec{r}) \hat{\Psi}_{\sigma'}^\dagger(\vec{r}') u(\vec{r} - \vec{r}') \hat{\Psi}_{\sigma'}(\vec{r}') \hat{\Psi}_{\sigma}(\vec{r}) \quad (2.22)$$

2.3 Example of well-known Hamiltonians

2.3.1 The Jellium Model

This describes a system of N interacting electrons, which are placed within a uniform background of positive charge, so that the whole system is charge neutral. In other words, it is as if we “smear” out the nuclei into a cloud of uniform positive charge. This greatly simplifies things, since the resulting system is invariant to any translations, instead of being invariant only to lattice translations. As a result, the logical one-particle basis are planewaves $\alpha = (k, \sigma)$ instead of more complicated Bloch states (note: r, p, k, \dots are all understood to be vectors, but I will not put arrows on them, except in the final expressions).

In the first quantization, the Hamiltonian for this system is:

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_{backg} + \mathcal{H}_{el-backg}$$

where the electronic Hamiltonian is:

$$\mathcal{H}_{el} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} u(r_i - r_j) \quad (2.23)$$

where we will assume a so-called screened Coulomb interaction

$$u(r) = \frac{e^2}{r} e^{-\mu r}$$

(at the end we can take $\mu \rightarrow 0$, if we want the usual, unscreened Coulomb interaction).

The background has a uniform positive density $n(r) = N/V$, and its energy is:

$$\mathcal{H}_{backg} = \frac{1}{2} \int dr \int dr' n(r) u(r - r') n(r') = \frac{N^2}{2V} u_{q=0}$$

since $\int dr = V$. From now on, I will denote the $q = 0$ Fourier component of the interaction as u_0 . Since $u_q = \int dr e^{-i\vec{q}\vec{r}} u(r) = 4\pi e^2 / (q^2 + \mu^2) \rightarrow u_0 = 4\pi e^2 / \mu^2 \dots$ and you see that we need a finite μ , at least for the time being.

The electron-background interactions are described by:

$$\mathcal{H}_{el-backg} = - \sum_{i=1}^N \int dr n(r) u(r - r_i) = - \frac{N^2}{V} u_0$$

since $\sum_i 1 = N$. So things simplify considerably because of the ‘‘jellium’’ assumption and we find:

$$\mathcal{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} u(r_i - r_j) - \frac{N^2}{2V} u_0$$

We now go to the second quantization, and use the (k, σ) basis, to find:

$$\mathcal{H} = \sum_{k, \sigma} \frac{\hbar^2 k^2}{2m} c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{2V} \sum_{\substack{k, k' \\ \sigma, \sigma'}} \sum_q u_q c_{k+q, \sigma}^\dagger c_{k'-q, \sigma'}^\dagger c_{k', \sigma'} c_{k\sigma} - \frac{N^2}{2V} u_0$$

Let us consider the $q = 0$ contribution from the electron-electron interaction:

$$\frac{u_0}{2V} \sum_{\substack{k, k' \\ \sigma, \sigma'}} c_{k, \sigma}^\dagger c_{k', \sigma'}^\dagger c_{k', \sigma'} c_{k\sigma} = \frac{u_0}{2V} \sum_{\substack{k, k' \\ \sigma, \sigma'}} c_{k, \sigma}^\dagger c_{k\sigma} c_{k', \sigma'}^\dagger c_{k', \sigma'} = \frac{u_0}{2V} N^2$$

Here, in the second equality we use the fact that $(k\sigma) \neq (k', \sigma')$ because if they are equal, $c_{k\sigma} c_{k\sigma} = 0$. As a result, we just (anti)commuted $c_{k\sigma}$ past the two other operators. In the last equality, we used the fact that $\sum_{k\sigma} c_{k, \sigma}^\dagger c_{k\sigma} = N$, since the system contains N electrons (strictly speaking, the condition $(k\sigma) \neq (k', \sigma')$ means that we have $N(N-1)$ instead of N^2 , but in the thermodynamic limit $N \rightarrow \infty$, this makes no difference). So we see that this exactly cancels the term left from the backg. and el-backg Hamiltonians (so we are no longer troubled even if $\mu \rightarrow 0$), and we obtain **the jellium model Hamiltonian**:

$$\mathcal{H} = \sum_{\vec{k}, \sigma} \frac{\hbar^2 k^2}{2m} c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + \frac{1}{2V} \sum_{\substack{\vec{k}, \vec{k}' \\ \sigma, \sigma'}} \sum_{\vec{q} \neq 0} u_{\vec{q}} c_{\vec{k}+\vec{q}, \sigma}^\dagger c_{\vec{k}'-\vec{q}, \sigma'}^\dagger c_{\vec{k}', \sigma'} c_{\vec{k}\sigma} \quad (2.24)$$

Note: this looks the same whatever the interaction happens to be. For instance, we may need to consider short-range interactions $u(\vec{r}) = U\delta(\vec{r}) \rightarrow u_{\vec{q}} = U$.

2.3.2 The Hubbard model

In this case, we start with atoms placed on a regular lattice, and use a basis of Wannier orbitals as our one-particle basis. (Wannier orbitals are eigenfunctions which are strongly localized about individual lattice sites. You can think of them almost as being the atomic orbitals of the isolated atom – except that some corrections are needed to insure that they are all orthogonal to one another). In this case, $\alpha = (i, n, \sigma)$, where i indicates the lattice site where the orbital is localized (spatial location \vec{R}_i), n are the quantum numbers for the type of orbital (for instance, $1s$ or $2p_z$) and σ is the spin. Then

$$\langle \vec{r}, \sigma | i, n, \sigma' \rangle = \delta_{\sigma, \sigma'} \phi_n(\vec{r} - \vec{R}_i)$$

Low-energy approximation: we are generally interested only in contributions from a particular set of orbitals – the other ones are either all filled, or all empty and far enough from the Fermi energy that their occupation number never changes. As a result, we can ignore all terms having to do with operators corresponding to these other orbitals, and approximate:

$$\hat{\Psi}_\sigma(\vec{r}) \approx \sum_i \phi(r - R_i) a_{i\sigma}; \quad \hat{\Psi}_\sigma^\dagger(\vec{r}) \approx \sum_i \phi^*(r - R_i) a_{i\sigma}^\dagger;$$

where from now on, I will no longer write explicitly the index n of the orbital of interest, since it is always the same number. We say that $a_{i\sigma}^\dagger$ creates an electron with spin σ at site i (which of course,

means that it adds an electron with spin σ in the specific orbital of interest, of the atom at site i). In this basis, the typical electronic Hamiltonian (2.23) becomes, in second quantization:

$$\mathcal{H} = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{\substack{i_1, i_2, i_3, i_4 \\ \sigma, \sigma'}} u_{i_1 i_2 i_3 i_4} a_{i_1 \sigma}^\dagger a_{i_2 \sigma'}^\dagger a_{i_3 \sigma'} a_{i_4 \sigma}$$

where, from definitions (2.7) and (2.9):

$$t_{ij} = \int d\vec{r} \phi^*(\vec{r} - \vec{R}_i) \left(\frac{\hbar^2}{2m} \nabla^2 \right) \phi(\vec{r} - \vec{R}_j)$$

and

$$u_{i_1 i_2 i_3 i_4} = \int d\vec{r} \int d\vec{r}' \phi^*(\vec{r} - \vec{R}_1) \phi^*(\vec{r}' - \vec{R}_2) u(\vec{r} - \vec{r}') \phi(\vec{r}' - \vec{R}_3) \phi(\vec{r} - \vec{R}_4)$$

and I used explicitly the fact that the kinetic energy and Coulomb interaction are independent of spin (Note: this is not automatically always true. One may have terms, for instance from spin-orbit interactions, which have non-trivial spin dependence.)

Since the orbitals are strongly localized about their atomic site, we can see that the largest contributions in the kinetic energy come when $i = j$ or i and j are nearest neighbors (denoted by $\langle i, j \rangle$). The further apart the atoms are, the smaller the overlap between the orbitals. If we keep only the largest terms, we find:

$$\mathcal{H} = -t \sum_{\langle i, j \rangle} a_{i\sigma}^\dagger a_{j\sigma} + \frac{U}{2} \sum_{i, \sigma, \sigma'} a_{i\sigma}^\dagger a_{i\sigma'}^\dagger a_{i\sigma'} a_{i\sigma}$$

(note: I discarded a term of the form $\epsilon \sum_i a_{i\sigma}^\dagger a_{i\sigma}$ coming from $i = j$ contribution in the kinetic energy, since this is just a constant proportional to the number of electrons. If we had atoms of various species, then the value of ϵ_i would vary for each site, and in this case such a term would be non-trivial and we would keep it. But for identical atoms, it can be discarded because it is trivial).

Finally, in the interaction term we must have $\sigma \neq \sigma'$, since $a_{i\sigma} a_{i\sigma} = 0$. We can then rearrange that term by commuting $a_{i\sigma}$ past the σ' operators, and rewriting it in terms of $\hat{n}_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$ (we assume spins 1/2):

$$\mathcal{H} = -t \sum_{\langle i, j \rangle} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (2.25)$$

This is the famous Hubbard Hamiltonian. t is called the nearest-neighbor hopping matrix, and U is the on-site Coulomb repulsion, and measures how strong is the repulsion between two electrons placed at the same site (according to Pauli, since they are in the same orbital of the same atom, they must have different spin projections).

Of course, this model can be extended to include hopping to second-nearest neighbors etc, and also longer-range interaction terms, between atoms which are at different neighboring sites. Another type of generalization is to multiple orbitals. If, for example, we have a Wannier orbital or p -type, i.e. three-degenerate, then we would have 6 states associated with each atom (3 orbitals x 2 spin projections), and since these orbitals are degenerate, we would need to keep all of them in the Hamiltonian. In this case, we have extra indices to indicate which of the three orbitals is involved, and hopping will strongly depend on the combination of orbitals involved (how are they oriented with respect to one another). So things can quickly become very complicated, it all depends on the complexity of the material we are trying to describe. Even the Hubbard Hamiltonian of Eq. (2.25) is not yet understood (except in some asymptotic cases), and this after over 40 years of study.

2.3.3 Electron-phonon interactions

In the two previous models, we assumed that the lattice is “inert”, i.e. the nuclei are not moving. Of course, in reality they oscillate about their equilibrium positions, and these oscillations are described by phonons. Since there are interactions between the nuclei and electrons, this motions of the nuclei will have an effect on the behavior of the electrons, described by so-called electron-phonon interactions.

You should know all about phonons from Phys502. I will summarize a few formulae here, to make it easier to discuss this topic. If you’re not familiar with phonons, ask me for some reading material – it is a straightforward topic that you can learn on your own.

If the unit cell contains r atoms, there are $3r$ phonon modes (I assume 3D motion), with dispersion $\hbar\omega_j(\vec{q})$, $j = 1, \dots, 3r$ and \vec{q} in the first Brillouin zone. 3 of these are always acoustic modes, with $\omega_j(\vec{q} \rightarrow 0) \rightarrow 0$, while the other ones are optical modes, with a finite value of $\omega_j(0)$. If we denote by $b_{\vec{q}}^\dagger$ the creation operator of a mode- j phonon with momentum \vec{q} , then the displacements of the atoms from their equilibrium positions, $\vec{u}_{n\alpha} = \vec{R}_{n\alpha} - \vec{R}_{n\alpha}^{(0)}$ are

$$\vec{u}_{n\alpha} = \frac{1}{\sqrt{NM_\alpha}} \sum_{j=1}^{3r} \sum_{\vec{q}} \sqrt{\frac{\hbar}{2\omega_j(\vec{q})}} \vec{c}_\alpha^{(j)}(\vec{q}) e^{i\vec{q}\cdot\vec{R}_n} (b_{j,-\vec{q}}^\dagger + b_{j\vec{q}}) \quad (2.26)$$

This looks complicated, but the meaning is straightforward: the $\vec{c}_\alpha^{(j)}(\vec{q})$ are just some numbers which show us the amplitudes of motion when various atoms are excited (i.e., in which direction will the atom move if that particular mode is excited. If you remember the discussion for the SHO, the displacement operator is proportional to $b + b^\dagger$, which is what we have here as well, but Fourier transformed. Finally, all those multiplication constants depending on the mass M_α of the various species of atoms in the basis, and the dispersion $\hbar\omega_j(\vec{q})$ of various modes, are just related to how we chose to define and normalize the c numbers).

Now let us consider additional terms to the Hamiltonian we can get from electron-phonon interactions. In first quantization, these are described by

$$\hat{V}_{el-ion} = \sum_{i=1}^N \sum_{n,\alpha} V_\alpha(\vec{r}_i - \vec{R}_{n,\alpha}) \approx \sum_{i=1}^N \sum_{n,\alpha} V_\alpha(\vec{r}_i - \vec{R}_{n,\alpha}^{(0)}) - \sum_{i=1}^N \sum_{n,\alpha} \vec{u}_{n,\alpha} \frac{\partial V_\alpha(\vec{r}_i - \vec{R}_{n,\alpha})}{\partial \vec{R}_{n,\alpha}}$$

where we just performed a Taylor expansion in $\vec{R}_{n\alpha} = \vec{R}_{n\alpha}^{(0)} + \vec{u}_{n\alpha}$, assuming small displacements $\vec{u}_{n\alpha}$ of the atoms from their equilibrium positions.

The first term in this equation is just the interaction of the electrons with the static, “fixed” lattice. This part is already included in the electronic Hamiltonians we have discussed. The second term is the extra part describing electron-phonon interaction. We already know how the $\vec{u}_{n,\alpha}$ depend on the phonon creation and annihilation operators. Let us now write this in the second quantization. Since we have a crystal, we know that the one-electron basis consists of bands separated by gaps. Let me use the index (n, \vec{k}, σ) , where n is the band index, \vec{k} is the momentum, and σ is the spin. Then, we have:

$$\mathcal{H}_{el-ph} = \sum_{\substack{n,k,\sigma \\ n',k',\sigma'}} \langle n, k, \sigma | \dots | n', k', \sigma' \rangle c_{n,k,\sigma}^\dagger c_{n',k',\sigma'}$$

where

$$\langle n, k, \sigma | \dots | n', k', \sigma' \rangle = - \int d\vec{r} \phi_{nk\sigma}^*(\vec{r}) \sum_{n,\alpha} \vec{u}_{n,\alpha} \frac{\partial V_\alpha(\vec{r} - \vec{R}_{n,\alpha})}{\partial \vec{R}_{n,\alpha}} \phi_{n'k'\sigma'}(\vec{r})$$

To calculate this, we express the potential V in terms of its Fourier transform, $V_\alpha(\vec{r} - \vec{R}_{n,\alpha}) = \frac{1}{V} \sum_Q e^{i\vec{Q}(\vec{r} - \vec{R}_{n,\alpha})} V_{\vec{Q}}$; the gradient is now trivial to take, and we are left with:

$$\langle n, k, \sigma | \dots | n', k', \sigma' \rangle = i \sum_{n,\alpha} \vec{Q} \cdot \vec{u}_{n\alpha} \frac{1}{V} \sum_Q e^{-i\vec{Q}\vec{R}_{n,\alpha}} V_{\vec{Q}} \int d\vec{r} \phi_{nk\sigma}^*(\vec{r}) e^{i\vec{Q}\vec{r}} \phi_{n'k'\sigma'}(\vec{r})$$

To do this integral, remember that any Bloch state can be written as

$$\phi_{nk\sigma}(\vec{r}) = \frac{e^{i\vec{k}\vec{r}}}{\sqrt{V}} u_{n\vec{k}}(\vec{r}) \chi_\sigma$$

where $u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r} + \vec{R}_n)$ is periodic with respect to lattice translations. From this, since the potential is independent of spin and $\chi_\sigma^T \chi_{\sigma'} = \delta_{\sigma\sigma'}$, it follows that $\sigma = \sigma'$: the electron-phonon interaction cannot change the electron spin. The integral can now be evaluated by breaking the integral over the whole crystal into a sum of integrals over each individual unit cell:

$$\int d\vec{r} \frac{e^{-i\vec{k}\vec{r}}}{\sqrt{V}} u_{n\vec{k}}^*(\vec{r}) e^{i\vec{Q}\vec{r}} \frac{e^{i\vec{k}'\vec{r}}}{\sqrt{V}} u_{n'\vec{k}'}(\vec{r}) = \sum_m \int_{\text{unit-cell}} d\vec{\rho} \frac{e^{-i\vec{k}(\vec{\rho} + \vec{R}_m)}}{\sqrt{V}} u_{n\vec{k}}^*(\vec{\rho}) e^{i\vec{Q}(\vec{\rho} + \vec{R}_m)} \frac{e^{i\vec{k}'(\vec{\rho} + \vec{R}_m)}}{\sqrt{V}} u_{n'\vec{k}'}(\vec{\rho})$$

But

$$\sum_m e^{i(-\vec{k} + \vec{Q} + \vec{k}')\vec{R}_m} = N \sum_G \delta_{\vec{G}, -\vec{k} + \vec{Q} + \vec{k}'}$$

where $N = V/\Omega$ is the total no. of unit cells, Ω is the unit cell volume, and the \vec{G} are the reciprocal lattice vectors. Finally, when we express the displacements $\vec{u}_{n\alpha}$ in terms of bosonic operators (see Eq. (2.26)), this will leave us with one more sum over all lattice vectors of the type:

$$\sum_n e^{i(\vec{q} - \vec{Q})\vec{R}_n} = N \sum_{G'} \delta_{\vec{G}', \vec{q} - \vec{Q}}$$

where \vec{q} is the momentum carried by phonons, and \vec{Q} was the Fourier component of the potential. So up to a reciprocal lattice vector, these two momenta are equal. Also, let me denote by:

$$\alpha_{\vec{G}; n\vec{k}; n'\vec{k}'} = \frac{1}{\Omega} \int_{\text{unit-cell}} d\vec{\rho} e^{i\vec{G}\vec{\rho}} u_{n\vec{k}}^*(\vec{\rho}) u_{n'\vec{k}'}(\vec{\rho}) \quad (2.27)$$

which can be calculated if the Bloch wavefunctions are known - they are just some numbers. In general, one makes the assumption that these integrals are negligible unless $n = n'$, i.e. that electron-phonon interactions cannot excite an electron from one band to a different band. This is usually justified by the fact that the typical phonon energies are much smaller than gaps between bands - but in materials where this is not true, one must keep inter-band transitions as well. Let us keep the whole expression, for completeness.

Putting all these pieces together, we find that a typical electron-phonon interaction Hamiltonian has the general form:

$$\mathcal{H}_{el-ph} = \frac{1}{N} \sum_{\substack{k,G,q,j \\ n,n',\sigma}} v_{k,G,q,j;n,n'} \left(b_{j,-\vec{q}}^\dagger + b_{j\vec{q}} \right) c_{n,\vec{k}+\vec{q}+\vec{G},\sigma}^\dagger c_{n',\vec{k},\sigma} \quad (2.28)$$

where I've thrown all multiplying constants in the $v_{k,G,q,j;n,n'}$.

This Hamiltonian describes processes where an electron in band n' and momentum \vec{k} either absorbs a phonon of mode j with momentum \vec{q} or emits a phonon of mode j with momentum $-\vec{q}$, and as a result it changes its state to one in the band n , with momentum $\vec{k} + \vec{q} + \vec{G}$, and same spin. Note that since in a crystal, momentum conservation is defined up to a reciprocal lattice vector, the crystal momentum is indeed conserved. As I said, one mostly considers only inter-band processes, where $n = n'$. Also, if we keep only terms with $\vec{G} = 0$, we have the usual conservation of the momentum. The processes where $\vec{G} \neq 0$ are called Umklapp processes.

If we ignore Umklapp processes, and assume that there is a single phonon mode (there are always more than one, but depending on the material of interest, one mode may interact a lot more strongly with the electrons, than others, so we can ignore the other ones to first order), and ignore inter-band processes, we get a much simpler form:

$$\mathcal{H}_{el-ph} = \frac{1}{\sqrt{N}} \sum_{\vec{k}, \vec{q}, \sigma} v_{\vec{k}, \vec{q}} (b_{-\vec{q}}^\dagger + b_{\vec{q}}) c_{\vec{k}+\vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma}$$

where I no longer specify the electronic band and the phonon mode: we understand that they are the ones of interest (i.e., the band containing the Fermi level, and the phonon mode most strongly coupled to electrons in this band). We'll use this simpler form when we discuss diagrammatics.

Finally, in some cases one can assume that $v_{\vec{k}, \vec{q}} = g$ is a constant. In this case, one can Fourier transform back to real space, and find out a specially simple electron-phonon interaction, called the Holstein model:

$$\mathcal{H}_{\text{Holstein}} = \frac{g}{\sqrt{N}} \sum_{\vec{k}, \vec{q}, \sigma} (b_{-\vec{q}}^\dagger + b_{\vec{q}}) c_{\vec{k}+\vec{q}, \sigma}^\dagger c_{\vec{k}, \sigma} = g \sum_n (b_n^\dagger + b_n) c_{n\sigma}^\dagger c_{n\sigma}$$

where I assumed a one-atom basis, and used the definition $c_{n\sigma} = \sum_k \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} c_{\vec{k}, \sigma}$ for annihilation of an electron at site n with spin σ , and similar relations for the b 's. The physics described by this term is simply that if there are electrons at site n (in which case the no. operator $c_{n\sigma}^\dagger c_{n\sigma}$ will give a non-zero contribution), then that atom will be displaced from its equilibrium position by some amount proportional to the no. of electrons present. This is to be expected, since an atom with a different charge will interact differently with its neighboring (usually charged) atoms, and so it will have a new equilibrium position in the lattice.