Notes on nonrelativistic systems

"Box" normalization and discrete wavevectors

So far we have studied systems of infinite size, which makes the wavevectors continuous (see Ch. 5 in JOA[1]). Alternatively, it can be convenient to instead consider a system of large but finite size. We take the system to be the inside of a large box with sides of length L_x, L_y, and L_z with volume $V = L_x L_y L_z$. This brings up the question of boundary conditions. As long as one restricts attention to bulk properties of macroscopically large systems, one can impose the boundary conditions that are most convenient mathematically, which typically are periodic boundary conditions (PBC's). (Of course, if one wanted to study properties of the system near the boundaries this would not be a valid choice of BC's.)

Consider nonrelativistic free particles (bosons or fermions). Omitting possible spin degrees of freedom for now, the eigenfunctions of the free-particle Schrödinger equation only have a spatial part, which are plane waves labeled by a wavevector $\boldsymbol{k}$,

$$\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{1}$$

(the prefactor $1/\sqrt{V}$ ensures that these wavefunctions are normalized). Imposing PBC's in the x direction, we have

$$\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \phi_{\boldsymbol{k}}(\boldsymbol{r} + L_x \hat{e}_x) \tag{2}$$

which gives $\boldsymbol{k}\cdot L_x\hat{e}_x = 2\pi n_x$, where n_x is an arbitrary integer. Thus the allowed values of k_x take the form

$$k_x = \frac{2\pi n_x}{L_x}. \tag{3}$$

Similarly, imposing PBC's in the y and z directions gives

$$k_y = \frac{2\pi n_y}{L_y}, \tag{4}$$

$$k_z = \frac{2\pi n_z}{L_z}, \tag{5}$$

with n_y and n_z arbitrary integers. We see that the allowed $\boldsymbol{k}$-vectors form a discrete set rather than a continuum.

Let us now expand the field operator in the complete set of plane waves:

$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} a_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{6}$$

Note that because the allowed $\boldsymbol{k}$-vectors are discrete, there is a sum instead of an integral in this expression. For concreteness, let's assume that the particles created and annihilated

[1] JOA = the lecture notes for TFY4210 by Jens Oluf Andersen, spring 2011.

by the field operators are bosons. Then we have the equal-time commutation relations

$$[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = \delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{7}$$
$$[\psi(\boldsymbol{r}), \psi(\boldsymbol{r}')] = [\psi^\dagger(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = 0. \tag{8}$$

These are satisfied if the a-operators satisfy the equal-time commutation relations

$$[a_{\boldsymbol{k}}, a^\dagger_{\boldsymbol{k}'}] = \delta_{\boldsymbol{k},\boldsymbol{k}'}, \tag{9}$$
$$[a_{\boldsymbol{k}}, a_{\boldsymbol{k}'}] = [a^\dagger_{\boldsymbol{k}}, a^\dagger_{\boldsymbol{k}'}] = 0, \tag{10}$$

where

$$\delta_{\boldsymbol{k},\boldsymbol{k}'} = \begin{cases} 1 & \text{if } \boldsymbol{k} = \boldsymbol{k}', \\ 0 & \text{if } \boldsymbol{k} \neq \boldsymbol{k}' \end{cases} \tag{11}$$

is called the Kronecker delta function. (In contrast, note that the corresponding commutation relations for continuous $\boldsymbol{k}$-vectors involved the Dirac delta function $\delta(\boldsymbol{k}-\boldsymbol{k}')$.) For example, let's verify this for (7):

$$[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = \frac{1}{V}\sum_{\boldsymbol{k},\boldsymbol{k}'} e^{i\boldsymbol{k}\cdot\boldsymbol{r} - i\boldsymbol{k}'\cdot\boldsymbol{r}'} \underbrace{[a_{\boldsymbol{k}}, a^\dagger_{\boldsymbol{k}'}]}_{\delta_{\boldsymbol{k},\boldsymbol{k}'}} = \frac{1}{V}\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}. \tag{12}$$

From (3) it follows that adjacent values of k_x differ by $2\pi/L_x \equiv \Delta k_x$. Similarly, $\Delta k_y = 2\pi/L_y$ and $\Delta k_z = 2\pi/L_z$. Thus we can write

$$[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = \sum_{\boldsymbol{k}} \frac{\Delta k_x \Delta k_y \Delta k_z}{(2\pi)^3} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \tag{13}$$

where we also used $V = L_x L_y L_z$. We are interested in systems for which L_x, L_y, L_z are each macroscopically large (and thus so is the volume V). In this limit Δk_x, Δk_y, and $\Delta k_z \to 0$, so we can approximate the sum by an integral:

$$\sum_{\boldsymbol{k}} \Delta k_x \Delta k_y \Delta k_z f(\boldsymbol{k}) \overset{V\to\infty}{\to} \int dk_x dk_y dk_z f(\boldsymbol{k}) = \int d^3k f(\boldsymbol{k}). \tag{14}$$

Thus we find

$$[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r}')] = \int \frac{d^3k}{(2\pi)^3} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = \delta(\boldsymbol{r}-\boldsymbol{r}'). \quad \text{Q.E.D.} \tag{15}$$

Next, let us express the kinetic energy operator

$$H_0 = \int_V d^3r \, \frac{\hbar^2}{2m} \nabla\psi^\dagger(\boldsymbol{r}) \cdot \nabla\psi(\boldsymbol{r}) \tag{16}$$

in terms of the a-operators. Inserting (6) and its h.c. and applying the ∇'s, we get

$$\begin{aligned} H_0 &= \frac{1}{V}\frac{\hbar^2}{2m}\int_V d^3r \sum_{\boldsymbol{k},\boldsymbol{k'}}(-i\boldsymbol{k})e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}a^\dagger_{\boldsymbol{k}}\cdot(i\boldsymbol{k'})e^{i\boldsymbol{k'}\cdot\boldsymbol{r}}a_{\boldsymbol{k'}} \\ &= \frac{\hbar^2}{2m}\sum_{\boldsymbol{k},\boldsymbol{k'}}\boldsymbol{k}\cdot\boldsymbol{k'}a^\dagger_{\boldsymbol{k}}a_{\boldsymbol{k'}}\underbrace{\frac{1}{V}\int_V d^3x\, e^{-i(\boldsymbol{k}-\boldsymbol{k'})\cdot\boldsymbol{r}}}_{\delta_{\boldsymbol{k},\boldsymbol{k'}}} \\ &= \sum_{\boldsymbol{k}}\frac{\hbar^2\boldsymbol{k}^2}{2m}\,a^\dagger_{\boldsymbol{k}}a_{\boldsymbol{k}}. \end{aligned} \tag{17}$$

If the particles have spin, we need to specify the spin state as well to have a full specification of a single-particle state. Let us consider electrons, which have spin 1/2. Using the eigenstates of the spin along the z axis, with eigenvalues $\sigma = \pm 1/2$, as our spin basis, the expansion (6) is generalized to

$$\psi_\sigma(\boldsymbol{r}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}} a_{\boldsymbol{k}\sigma}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{18}$$

Furthermore, since electrons are fermions, the commutators in (7)-(10) must be replaced by anticommutators. For example, the equal-time anticommutation relations for the a-operators creating or annihilating electrons with a definite wavevector and spin projection read

$$\{a_{\boldsymbol{k}\sigma}, a^\dagger_{\boldsymbol{k'}\sigma'}\} = \delta_{\boldsymbol{k},\boldsymbol{k'}}\delta_{\sigma\sigma'}, \tag{19}$$

$$\{a_{\boldsymbol{k}\sigma}, a_{\boldsymbol{k'}\sigma'}\} = \{a^\dagger_{\boldsymbol{k}\sigma}, a^\dagger_{\boldsymbol{k'}\sigma'}\} = 0, \tag{20}$$

Finally, the kinetic energy operator becomes

$$H_0 = \sum_\sigma \int_V d^3r\, \frac{\hbar^2}{2m}\nabla\psi^\dagger_\sigma(\boldsymbol{r})\cdot\nabla\psi_\sigma(\boldsymbol{r}) \tag{21}$$

$$= \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2\boldsymbol{k}^2}{2m}\,a^\dagger_{\boldsymbol{k}\sigma}a_{\boldsymbol{k}\sigma}. \tag{22}$$

Note that by doing an integration by parts and using the PBC's to get rid of the boundary terms, (21) can be rewritten as

$$H_0 = \sum_\sigma \int d^3r\, \psi^\dagger_\sigma(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_\sigma(\boldsymbol{r}). \tag{23}$$

Similarly, by removing the spin subscripts and spin summation here one gets the analogous rewritten version of Eq. (16).

Nonrelativistic systems of many identical material particles

When we motivated the introduction of quantum field theory for relativistic particles earlier in the course, one of the arguments we made was that in relativistic systems, particles

can be created or annihilated, making it impossible to describe the system in terms of a wavefunction $\Psi(x_1, \ldots, x_N)$ of a fixed number N of particles. Thus a different approach was clearly needed, and this approach, quantum field theory, can be formulated in terms of creation and annihilation operators. The formalism based on such operators is often called **second quantization**.

On the other hand, consider instead a nonrelativistic system of particles, for example electrons in a solid. As creation/annihilation processes that change their number are absent, such a system could therefore be described in terms of the standard quantum mechanical formalism based on (many-particle) wavefunctions. This wavefunction formalism is often referred to as **first quantization**, especially when it is compared and contrasted with the second quantization formalism.[2]

Let us first discuss the first quantization formalism a bit. A system of N identical particles can be described by a many-particle (aka many-body) wavefunction $\Psi(x_1, \ldots, x_N; t)$ which is symmetric (antisymmetric) under particle interchange if the particles are bosons (fermions):

$$\Psi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N; t) = \pm\Psi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N; t) \tag{24}$$

where on the rhs we have interchanged the coordinates of particles i and j. The upper sign is for bosons, the lower sign for fermions. We emphasize that if the particles have spin the symbol x includes the spin projection along some axis as well as the position vector of the particle, i.e. $x = (\boldsymbol{r}, \sigma)$, so in this case an interchange of coordinates involves interchanging both the spatial and spin coordinates of two particles. (Also note that unlike the notation we used earlier especially for relativistic systems, here and in the following we do not include the time coordinate t as part of the symbol x.) The time-independent Schrödinger equation is

$$H\Phi_n(x_1, x_2, \ldots, x_N) = E_n\Phi_n(x_1, x_2, \ldots, x_N) \tag{25}$$

where Φ_n and E_n are eigenfunctions and eigenvalues of the Hamiltonian H, which can be written

$$H = H_0 + H_{\text{int}}, \tag{26}$$

where H_0 is the noninteracting part of the Hamiltonian and H_{int} is the interacting part. If the particles are free, H_0 is just the kinetic energy operator,

$$H_0 = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \right) \nabla_i^2. \tag{27}$$

Otherwise H_0 could also include the coupling to an external potential (we'll come back to this later). Furthermore, we will assume that the interaction part H_{int} is a two-particle interaction, which can be written on the form

$$H_{\text{int}} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} v(x_i, x_j). \tag{28}$$

[2]We won't go into the reasons behind the names of first and second quantization. We refer to Ch. 2 in Hatfield's "Quantum field theory of point particles and strings" for a nice discussion.

For example, electrons interact via the (spin-independent) Coulomb interaction given by $v(\boldsymbol{r}, \boldsymbol{r}') = e^2/4\pi\epsilon_0|\boldsymbol{r} - \boldsymbol{r}'|$. While we could study the system using this first quantization formalism based on many-particle wavefunctions and operators on the form (27) and (28), this formalism is very cumbersome compared to the alternative second quantization formalism, in which operators are expressed in terms of creation and annihilation operators that create or annihilate particles in specific single-particle states, and the many-particle basis states can be expressed in terms of creation operators acting on a "vacuum" state $|0\rangle$ containing no particles. For example, $|\Phi\rangle = a^\dagger_{\nu_1} a^\dagger_{\nu_2} a^\dagger_{\nu_3}|0\rangle$ is an example of a 3-particle basis state in the second quantization formalism; here $a^\dagger_\nu$ creates a particle in the single-particle state specified by the quantum numbers ν.

Using canonical quantization (introduced in JOA, Ch. 5) we have already seen what the kinetic energy operator H_0 looks like in the second quantization formalism; see Eqs. (16), (17), and (21)-(23). Let us therefore now consider what H_{int} looks like in the second quantization formalism. To do this we first go back to Exercise 5.6.3, where we found that the total number operator (which counts the total number of particles in the system) was given by

$$\hat{N} = \int d^3x \; \psi^\dagger(x)\psi(x). \tag{29}$$

It is natural to define the density operator $\rho(x)$ as

$$\hat{N} = \int d^3x \, \rho(x). \tag{30}$$

Comparison with Eq. (29) then gives

$$\rho(x) = \psi^\dagger(x)\psi(x) \tag{31}$$

as the 2nd-quantized representation of the density operator. On the other hand, the 1st-quantized representation of the density operator is

$$\rho(x) = \sum_{i=1}^{N} \delta(x - x_i), \tag{32}$$

as this picks up a nonzero contribution only for those values of x where the particles are, and furthermore gives the total particle number N when integrated over all x: $\int d^3x \, \rho(x) = \sum_{i=1}^{N} \int d^3x \, \delta(x - x_i) = N$.

Next note that the first-quantized representation of H_{int}, Eq. (28), can be written

$$H_{\text{int}} = \frac{1}{2}\left[\int dx \int dx' v(x, x')\rho(x)\rho(x') - \int dx \; v(x, x)\rho(x)\right] \tag{33}$$

with $\rho(x)$ given by (32). Proof: Inserting (32) gives

$$\begin{aligned}
&\frac{1}{2}\left[\int dx \int dx'\; v(x,x')\sum_i \delta(x-x_i)\sum_j \delta(x'-x_j) - \int dx\; v(x,x)\sum_i \delta(x-x_i)\right] \\
&= \frac{1}{2}\left[\sum_i\sum_j v(x_i,x_j) - \sum_i v(x_i,x_i)\right] = \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} v(x_i,x_j) = H_{\rm int}. \quad \text{QED.}
\end{aligned} \tag{34}$$

We can now find the second-quantized representation of (28) by using the second-quantized representation of $\rho(x)$, Eq. (31), in Eq. (33). This gives

$$\begin{aligned}
H_{\rm int} &= \frac{1}{2}\left[\int dx \int dx'\; v(x,x')\rho(x)\rho(x') - \int dx\; v(x,x)\rho(x)\right] \\
&= \frac{1}{2}\left[\int dx \int dx'\; v(x,x')\psi^\dagger(x)\underbrace{\psi(x)\psi^\dagger(x')}_{\text{rewrite}}\psi(x') - \int dx\; v(x,x)\psi^\dagger(x)\psi(x)\right]
\end{aligned} \tag{35}$$

Now we use that

$$[\psi(x),\psi^\dagger(x')]_r = \delta(x-x') \tag{36}$$

where we have defined

$$[A,B]_r = AB + rBA \tag{37}$$

In Eq. (36), $r=\pm 1$ for fermionic/bosonic field operators. This gives

$$\psi(x)\psi^\dagger(x') = -r\psi^\dagger(x')\psi(x) + \delta(x-x'). \tag{38}$$

We insert this for the product labeled "rewrite" in (35) and do the x' integration in the term with the Dirac delta function. This gives

$$\begin{aligned}
H_{\rm int} &= \frac{1}{2}\Bigg[-r\int dx \int dx'\; v(x,x')\psi^\dagger(x)\psi^\dagger(x')\psi(x)\psi(x') \\
&\quad + \underbrace{\int dx\; v(x,x)\psi^\dagger(x)\psi(x) - \int dx\; v(x,x)\psi^\dagger(x)\psi(x)}_{0}\Bigg] \\
&= -\frac{1}{2}r\int dx \int dx'\; v(x,x')\psi^\dagger(x)\psi^\dagger(x')\underbrace{\psi(x)\psi(x')}_{-r\psi(x')\psi(x)} \\
&= \frac{1}{2}\underbrace{(-r)^2}_{1}\int dx \int dx'\; v(x,x')\psi^\dagger(x)\psi^\dagger(x')\psi(x')\psi(x),
\end{aligned} \tag{39}$$

i.e. the second-quantized representation of $H_{\rm int}$ is

$$H_{\rm int} = \frac{1}{2}\int dx \int dx'\; \psi^\dagger(x)\psi^\dagger(x')v(x,x')\psi(x')\psi(x). \tag{40}$$

As an example, let us consider the Coulomb interaction between electrons. As electrons have spin $S = 1/2$, we have in this case $x = (\boldsymbol{r}, \sigma)$ with $\sigma = \pm 1/2$, so $\psi(x) = \psi_\sigma(\boldsymbol{r})$ and $\int d^3x = \sum_\sigma \int d^3r$. The Coulomb interaction is given by

$$v(x, x') = \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r} - \boldsymbol{r}'|} \equiv v(\boldsymbol{r} - \boldsymbol{r}'). \tag{41}$$

Eq. (40) gives

$$H_{\rm int} = \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \; \psi^\dagger_\sigma(\boldsymbol{r}) \psi^\dagger_{\sigma'}(\boldsymbol{r}') v(\boldsymbol{r} - \boldsymbol{r}') \psi_{\sigma'}(\boldsymbol{r}') \psi_\sigma(\boldsymbol{r}). \tag{42}$$

Let us rewrite this in terms of the momentum-spin single-particle basis $(\boldsymbol{k}, \sigma)$. Making use of (18), we get

$$\begin{aligned} H_{\rm int} \;\; = \;\; & \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} a^\dagger_{\boldsymbol{k}_1\sigma} a^\dagger_{\boldsymbol{k}_2\sigma'} a_{\boldsymbol{k}_3\sigma'} a_{\boldsymbol{k}_4\sigma} \\ & \cdot \frac{1}{V^2} \int d^3r \int d^3r' \; v(\boldsymbol{r} - \boldsymbol{r}') e^{-i(\boldsymbol{k}_1 - \boldsymbol{k}_4)\cdot \boldsymbol{r}} e^{-i(\boldsymbol{k}_2 - \boldsymbol{k}_3)\cdot \boldsymbol{r}'} \end{aligned} \tag{43}$$

Let us define $\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}'$ and change integration variables to $\boldsymbol{R}$ and $\boldsymbol{r}'$. The integrals then factorize as follows:

$$\frac{1}{V} \underbrace{\int d^3R \, v(\boldsymbol{R}) e^{-i(\boldsymbol{k}_1 - \boldsymbol{k}_4)\cdot \boldsymbol{R}}}_{\equiv v_{\boldsymbol{k}_1 - \boldsymbol{k}_4}} \cdot \underbrace{\frac{1}{V} \int d^3r' \, e^{-i(\boldsymbol{k}_2 - \boldsymbol{k}_3 + \boldsymbol{k}_1 - \boldsymbol{k}_4)\cdot \boldsymbol{r}'}}_{= \delta_{\boldsymbol{k}_1, \boldsymbol{k}_4 + \boldsymbol{k}_3 - \boldsymbol{k}_2}} \tag{44}$$

where $v_{\boldsymbol{q}}$ is the Fourier transform of $v(\boldsymbol{r})$. Doing the summation over $\boldsymbol{k}_1$ then gives

$$H_{\rm int} = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4} v_{\boldsymbol{k}_3 - \boldsymbol{k}_2} \; a^\dagger_{\boldsymbol{k}_4 + \boldsymbol{k}_3 - \boldsymbol{k}_2, \sigma} a^\dagger_{\boldsymbol{k}_2\sigma'} a_{\boldsymbol{k}_3\sigma'} a_{\boldsymbol{k}_4\sigma}. \tag{45}$$

Let us define new summation variables $\boldsymbol{k}$, $\boldsymbol{k}'$, and $\boldsymbol{q}$ by

$$\boldsymbol{k}_4 \equiv \boldsymbol{k}, \quad \boldsymbol{k}_3 \equiv \boldsymbol{k}', \quad \boldsymbol{k}_2 \equiv \boldsymbol{k}' - \boldsymbol{q}. \tag{46}$$

This gives

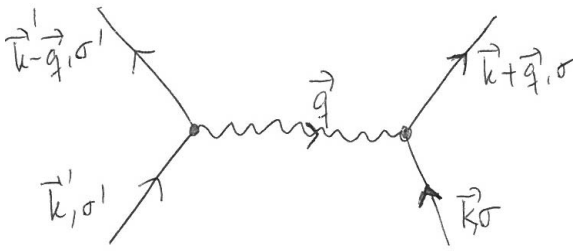
$$\boldsymbol{k}_4 + \boldsymbol{k}_3 - \boldsymbol{k}_2 \;\; = \;\; \boldsymbol{k} + \boldsymbol{q}, \tag{47}$$

$$\boldsymbol{k}_3 - \boldsymbol{k}_2 \;\; = \;\; \boldsymbol{q}. \tag{48}$$

Thus

$$H_{\rm int} = \frac{1}{2V} \sum_{\boldsymbol{q}} v_{\boldsymbol{q}} \sum_{\substack{\boldsymbol{k},\sigma \\ \boldsymbol{k}',\sigma'}} a^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} a^\dagger_{\boldsymbol{k}'-\boldsymbol{q},\sigma'} a_{\boldsymbol{k}'\sigma'} a_{\boldsymbol{k}\sigma}. \tag{49}$$

This expression describes scattering processes in which two electrons scatter by exchanging momentum $\boldsymbol{q}$. Before the scattering the electrons have momenta $\boldsymbol{k}$ and $\boldsymbol{k}'$, after the scattering the electrons have momenta $\boldsymbol{k}+\boldsymbol{q}$ and $\boldsymbol{k}'-\boldsymbol{q}$. Note that the total momentum $\boldsymbol{k}+\boldsymbol{k}'$ is conserved in the scattering process. This is a consequence of the translational invariance of the interaction, i.e. the fact that it only depends on $\boldsymbol{r}-\boldsymbol{r}'$, not on $\boldsymbol{r}$ and $\boldsymbol{r}'$ separately. Also note that since the Coulomb interaction (41) is spin-independent, the electrons spins are not affected by the scattering process. A diagrammatic representation of the scattering process is shown in the figure.



Mathematically, the scattering is described by the annihilation of the incoming electrons with momentum $\boldsymbol{k}$ and $\boldsymbol{k}'$ and the creation of the outgoing electrons with momentum $\boldsymbol{k}+\boldsymbol{q}$ and $\boldsymbol{k}'-\boldsymbol{q}$. For the Coulomb interaction, $v_{\boldsymbol{q}} \propto 1/|\boldsymbol{q}|^2$. The divergence of $v_{\boldsymbol{q}}$ at small $|\boldsymbol{q}|$ is due to the long-range nature of $v(\boldsymbol{r})$.

Basis transformations

So far in our discussion of second quantization we have only used two different single-particle basis sets, having quantum numbers $\boldsymbol{r}$ or $\boldsymbol{k}$ respectively, i.e. they consist of eigenfunctions of the position operator or of the momentum operator (equivalently the kinetic energy). For particles with spin, the wavefunction also contains a spin part, and so we also include the spin projection along the z direction as another quantum number in order to fully characterize the single-particle wavefunctions in each of these basis sets. For example, Eqs. (23) and (42) make use of the $(\boldsymbol{r},\sigma)$ basis set, while Eqs. (22) and (49) make use of the $(\boldsymbol{k},\sigma)$ basis set. While these two basis sets are often the most suitable and convenient to use, there can also be other systems for which it is preferable to use a different basis set. For example, if the electrons are subject to an external potential $u(x)$, it can be convenient to use the single-particle basis of eigenfunctions of the operator $-(\hbar^2/2m)\nabla^2+u(x)$. In the following we discuss how to relate creation/annihilation operators in one basis to creation/annihilation operators in another basis.

Let $|\alpha\rangle$ be the single-particle ket whose overlap with the position-spin eigenstate $|x\rangle$ is the single-particle wavefunction $\phi_\alpha(x)$, i.e.

$$\phi_\alpha(x) \equiv \langle x|\alpha\rangle. \tag{50}$$

For both bosonic and fermionic particles we can write

$$|\alpha\rangle = a_\alpha^\dagger|0\rangle \tag{51}$$

where $a_\alpha^\dagger$ is the creation operator for a particle in single-particle state α. Let us now consider a different single-particle basis set $\{\tilde{\phi}_{\tilde{\alpha}}(x)\}$ whose single-particle kets are denoted $|\tilde{\alpha}\rangle$. That is,

$$\tilde{\phi}_{\tilde{\alpha}}(x) \equiv \langle x|\tilde{\alpha}\rangle \tag{52}$$

with

$$|\tilde{\alpha}\rangle = a_{\tilde{\alpha}}^\dagger|0\rangle, \tag{53}$$

i.e. $a_{\tilde{\alpha}}^\dagger$ is the creation operator for a particle in the single-particle state $\tilde{\alpha}$. As a concrete example, $\{|\alpha\rangle\}$ could be the set of eigenstates of the kinetic-energy operator $-(\hbar^2/2m)\nabla^2$, while $\{|\tilde{\alpha}\rangle\}$ could be the eigenstates of the operator $-(\hbar^2/2m)\nabla^2 + u(x)$, where $u(x)$ is a external potential.

To transform between the two single-particle basis sets we use the resolution of the identity I in the single-particle Hilbert space:

$$I = \sum_\alpha |\alpha\rangle\langle\alpha| = \sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle\langle\tilde{\alpha}|. \tag{54}$$

Thus

$$a_\alpha^\dagger|0\rangle = |\alpha\rangle = \sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle\langle\tilde{\alpha}|\alpha\rangle = \sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle|\tilde{\alpha}\rangle = \sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle a_{\tilde{\alpha}}^\dagger|0\rangle \tag{55}$$

and thus

$$a_\alpha^\dagger = \sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle a_{\tilde{\alpha}}^\dagger. \tag{56}$$

Taking the adjoint of this equation gives the transformation rule for the annihilation operators:

$$a_\alpha = \sum_{\tilde{\alpha}}\langle\alpha|\tilde{\alpha}\rangle a_{\tilde{\alpha}}. \tag{57}$$

The inverse transformations can be derived in the same way (or more simply by interchanging α and $\tilde{\alpha}$ in the expressions so far):

$$a_{\tilde{\alpha}}^\dagger = \sum_\alpha\langle\alpha|\tilde{\alpha}\rangle a_\alpha^\dagger, \tag{58}$$

$$a_{\tilde{\alpha}} = \sum_\alpha\langle\tilde{\alpha}|\alpha\rangle a_\alpha. \tag{59}$$

From these results we can also find the transformation rules for the wavefunctions:

$$\phi_\alpha(x) = \langle x|\alpha\rangle = \langle x|\left(\sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle|\tilde{\alpha}\rangle\right) = \sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle\langle x|\tilde{\alpha}\rangle = \sum_{\tilde{\alpha}}\langle\tilde{\alpha}|\alpha\rangle\tilde{\phi}_{\tilde{\alpha}}(x), \tag{60}$$

and similarly

$$\tilde{\phi}_{\tilde{\alpha}}(x) = \sum_\alpha\langle\alpha|\tilde{\alpha}\rangle\phi_\alpha(x). \tag{61}$$

The basis transformations are unitary transformations. To see this, consider the matrix D defined by the matrix elements entering the transformations: $D_{\tilde{\alpha}\alpha} \equiv \langle\tilde{\alpha}|\alpha\rangle$. D is a unitary matrix, since

$$\begin{aligned}\delta_{\tilde{\alpha},\tilde{\beta}} &= \langle\tilde{\alpha}|\tilde{\beta}\rangle = \sum_\gamma \langle\tilde{\alpha}|\gamma\rangle\langle\gamma|\tilde{\beta}\rangle = \sum_\gamma \langle\tilde{\alpha}|\gamma\rangle\langle\tilde{\beta}|\gamma\rangle^* \\ &= \sum_\gamma D_{\tilde{\alpha}\gamma} D^*_{\tilde{\beta}\gamma} = \sum_\gamma D_{\tilde{\alpha}\gamma}(D^\dagger)_{\gamma\tilde{\beta}} = (DD^\dagger)_{\tilde{\alpha}\tilde{\beta}}, \quad \Rightarrow \quad DD^\dagger = I. \end{aligned} \tag{62}$$

The basis transformations preserve (anti-)commutation relations. In other words, the creation/annihilation operators in the new basis satisfy the same kinds of (anti-)commutation relations as the creation/annihilation operators in the old basis. Thus, for example, from the fact that $[a_\alpha, a^\dagger_{\alpha'}]_r = \delta_{\alpha\alpha'}$ (see Eq. (37)) it follows that

$$[a_{\tilde{\alpha}}, a^\dagger_{\tilde{\alpha}'}]_r = \sum_{\alpha,\alpha'} \langle\tilde{\alpha}|\alpha\rangle\langle\alpha'|\tilde{\alpha}'\rangle \underbrace{[a_\alpha, a^\dagger_{\alpha'}]_r}_{\delta_{\alpha\alpha'}} = \langle\tilde{\alpha}|\tilde{\alpha}'\rangle = \delta_{\tilde{\alpha},\tilde{\alpha}'}. \tag{63}$$

Similarly, it is easily shown that $[a_{\tilde{\alpha}}, a_{\tilde{\alpha}'}]_r = [a^\dagger_{\tilde{\alpha}}, a^\dagger_{\tilde{\alpha}'}]_r = 0$ just like the corresponding (anti-)commutators in the old basis.

The field operators $\psi(x)$ and $\psi^\dagger(x)$ are just the annihilation and creation operators corresponding to the position-spin basis set $\{|x\rangle\}$. (In other words, the field operators could more logically have been denoted by a_x and $a^\dagger_x$, but for some reason (probably mainly historical) this notation is not used for the position-spin basis.) Thus taking $\tilde{\alpha} = x$ in (58)-(59) and using (50) we get

$$\psi^\dagger(x) = \sum_\alpha \phi^*_\alpha(x)\, a^\dagger_\alpha, \tag{64}$$

$$\psi(x) = \sum_\alpha \phi_\alpha(x)\, a_\alpha. \tag{65}$$

Note that in (63) we used $\langle\tilde{\alpha}|\tilde{\alpha}'\rangle = \delta_{\tilde{\alpha},\tilde{\alpha}'}$, which is based on the assumption that the quantum numbers $\tilde{\alpha}$ can take a discrete set of values. That is not the case for the position-spin quantum number x, because the position quantum number $\boldsymbol{r}$ takes values from a continuous set. Therefore we have $\langle\boldsymbol{r}|\boldsymbol{r}'\rangle = \delta(\boldsymbol{r} - \boldsymbol{r}')$, a Dirac delta function. Thus we get

$$[\psi(x), \psi^\dagger(x)]_r = \delta(x - x'), \tag{66}$$

where $\delta(x - x') \equiv \delta(\boldsymbol{r} - \boldsymbol{r}')$ for spinless particles; otherwise $\delta(x - x') \equiv \delta_{\sigma\sigma'}\delta(\boldsymbol{r} - \boldsymbol{r}')$.

To check that Eqs. (64)-(65) are consistent with previous results, let us show that (64) implies (18). Thus $\alpha = (\boldsymbol{k}, \sigma')$ and $x = (\boldsymbol{r}, \sigma)$. The momentum-spin eigenfunctions are

$$\phi_\alpha(x) \equiv \langle x|\alpha\rangle = \langle\boldsymbol{r}, \sigma|\boldsymbol{k}, \sigma'\rangle = \underbrace{\langle\boldsymbol{r}|\boldsymbol{k}\rangle}_{V^{-1/2}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}} \underbrace{\langle\sigma|\sigma'\rangle}_{\delta_{\sigma,\sigma'}}. \tag{67}$$

Thus

$$\psi_\sigma(\boldsymbol{r}) = \sum_{\boldsymbol{k},\sigma'} \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \delta_{\sigma\sigma'} a_{\boldsymbol{k}\sigma'} = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} a_{\boldsymbol{k}\sigma}. \quad \text{QED.} \tag{68}$$

Finally, let us express the kinetic energy operator H_0 and the two-particle interaction H_{int} in terms of an arbitrary single-particle basis set. Inserting (64)-(65) into (40) immediately gives

$$H_{\text{int}} = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \left[\int \int dx dx' \; \phi^*_\alpha(x) \phi^*_\beta(x') v(x,x') \phi_\delta(x') \phi_\gamma(x) \right] a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma. \tag{69}$$

For the kinetic energy, starting from

$$H_0 = \int d^3x \, \psi^\dagger(x) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi(x) \tag{70}$$

we similarly get

$$H_0 = \sum_{\alpha,\beta} \left[\int dx \, \phi^*_\alpha(x) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_\beta(x) \right] a^\dagger_\alpha a_\beta. \tag{71}$$

(we emphasize that in both (69) and (71) the quantities inside square brackets are just c-numbers).

More on first vs. second quantization

(At this point in the lectures I decided to go into a bit more detail on the first vs. second quantization formalisms, and the relationship between them. The exercises for week 13 also deal with this.)

So far the way we introduced the second quantization formalism was via the field quantization ("canonical quantization") procedure introduced in Ch. 5 in JOA. Now we will discuss an alternative way of thinking about the second quantization formalism for nonrelativistic systems, and how it is connected to the first quantization formalism. These two formalisms are then alternative and equivalent ways of analyzing the same system. In each formalism we have representations for two types of objects: states $|\Psi\rangle$ and operators O. These objects are however rather abstract in nature. Much more concrete are matrix elements, $\langle\Psi'|O|\Psi\rangle$, since they are just ordinary numbers (c-numbers). All physically measurable quantities are expressible in terms of matrix elements. (Expectation values correspond to the special case $|\Psi\rangle = |\Psi'\rangle$.) One key point is that although the representations of states and operators are very different in first and second quantization, the matrix elements must of course take the same value regardless of which of the two formalisms one uses to calculate them. Furthermore, note that since an arbitrary many-particle state $|\Psi\rangle$ can be expressed as a linear combination of many-particle basis states $|\Phi_m\rangle$, i.e.

$$|\Psi\rangle = \sum_m f_m |\Phi_m\rangle, \tag{72}$$

where f_m are expansion coefficients, it suffices to consider matrix elements involving many-particle basis states only, i.e. matrix elements of the form

$$\langle \Phi_m | O | \Phi_n \rangle. \tag{73}$$

The many-particle basis states can in turn be constructed from single-particle states in a chosen single-particle basis set. We will first discuss how this is done in the first quantization formalism.

First quantization

In the first quantization formalism, the single-particle basis consists of eigenfunctions of a hermitian operator $\hat{o}$. Although not necessary, it is often convenient to take $\hat{o} = \hat{h}$, where $\hat{h}$ is the operator involved in the noninteracting part H_0 of the full Hamiltonian of the many-particle system. That is, $H = H_0 + H_{\rm int}$, with

$$H_0 = \sum_{i=1}^{N} \hat{h}_i \quad \text{where } \hat{h}_i = -\frac{\hbar^2}{2m}\nabla_i^2 + u(x_i) \tag{74}$$

where $u(x)$ is an external potential (which may be 0). We assume that we have found the eigenfunctions $\phi_\nu(x)$ and associated eigenvalues ϵ_ν for the single-particle problem defined by $\hat{o}$, i.e.

$$\hat{o}\phi_\nu(x) = \epsilon_\nu \phi_\nu(x). \tag{75}$$

Here ν is a set of quantum numbers which completely characterize the single-particle eigenstates ϕ_ν. These states form a complete and orthonormal set for expanding single-particle wavefunctions.

From these single-particle wavefunctions we can then construct many-particle wavefunctions with the the correct symmetry. These many-particle wavefunctions are eigenfunctions of the operator $\hat{O} = \sum_{i=1}^{N} \hat{o}_i$. For bosons the wavefunction must be symmetric and can be written on the form (the superscript S stands for "symmetric")

$$\Phi^{(S)}(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}\sqrt{\prod_k n_k!}} \sum_{P \in S_N} P\, \phi_{\nu_1}(x_1)\phi_{\nu_2}(x_2)\cdots\phi_{\nu_N}(x_N). \tag{76}$$

Here the sum is over all permutations P of the N coordinates $x_1, \ldots, x_N$. S_N is the set of all these permutations; there are $N!$ permutations in all. The prefactor has been chosen to make the state normalized to 1. The product $\prod_k n_k! = n_1!n_2!n_3!\ldots$ is over all single-particle states; n_k is the number of bosons in the single-particle state k. Note that for bosons there is no restriction in how many particles can be in the same single-particle state. Hence in this expression different indices ν_j can be identical. For example, if $\nu_3 = \nu_5$ (and all other indices are different from ν_3) the many-particle state would have two particles in the single-particle state ν_3, hence $n_{\nu_3} = 2$.

For fermions the wavefunction must be antisymmetric and can be written (the superscript A stands for "antisymmetric")

$$\Phi^{(A)}(x_1,\ldots,x_N)=\frac{1}{\sqrt{N!}}\sum_{P\in S_N}\mathrm{sgn}(P)\cdot P\;\phi_{\nu_1}(x_1)\phi_{\nu_2}(x_2)\cdots\phi_{\nu_N}(x_N). \tag{77}$$

Compared to the bosonic case, there are two differences: (1) The product over occupation numbers $n_k!$ in the prefactor is not there (this is because, as we will shortly see, for fermions n_k can only be 0 or 1 (otherwise the wavefunction will vanish), in which case $n_k!=1$ and thus this product doesn't have to be explicitly included), and (2) there is a factor $\mathrm{sgn}(P)$ inside the sum. This is the sign of the permutation P. A permutation has a *positive* (*negative*) sign if it can be arrived at by an *even* (*odd*) number of two-particle permutations (transpositions). For example, suppose we had 3 fermions. Let us consider the permutation $(123)\to(231)$. Any permutation can be written as a product of transpositions P_{jk}, each of which interchanges the numbers at position j and k. For example, we have $P_{13}(123)=(321)$ and $P_{12}(321)=(231)$. Hence we can write $(231)=P_{12}P_{13}(123)$. Thus this permutation can be written in terms of an even number of transpositions, and the sign of the permutation is therefore positive. Although the way to express a permutation in terms of transpositions is not unique, the evenness/oddness is unique, and hence the sign is also unique. In the example just considered, we could have written (check!) $(231)=P_{23}P_{13}P_{12}P_{23}(123)$, which involves four transpositions, again an even number.

The fermionic wavefunction in (77) can be written as a determinant (known as a *Slater* determinant):

$$\Phi^{(A)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_{\nu_1}(x_1) & \cdots & \phi_{\nu_1}(x_N)\\ \vdots & & \vdots\\ \phi_{\nu_N}(x_1) & \cdots & \phi_{\nu_N}(x_N)\end{vmatrix}. \tag{78}$$

Note that the determinant of a matrix vanishes if it contains identical rows and/or identical columns. Therefore the determinant (78) will vanish if $\nu_i=\nu_j$ for some $i\neq j$, i.e. it is not possible to put more than one fermion into a given single-particle state. The determinant will also vanish if $x_i=x_j$ for some $i\neq j$, i.e. it is not possible to bring two fermions with the same spin projection to the same point. These properties are known as the *Pauli exclusion principle*.

Given some collection of N (singly) occupied single-particle states, the fermionic many-particle wavefunction (78) constructed from them is defined only up to an overall sign. For example, consider a two-particle state, with two single-particle states (just call them 1 and 3) occupied. Then we could define the wavefunction either as

$$\Phi^{(A1)}=\frac{1}{\sqrt{2}}(\phi_1(x_1)\phi_3(x_2)-\phi_1(x_2)\phi_3(x_1), \tag{79}$$

or as

$$\Phi^{(A2)}=\frac{1}{\sqrt{2}}(\phi_3(x_1)\phi_1(x_2)-\phi_3(x_2)\phi_1(x_1))=-\Phi^{(A1)}. \tag{80}$$

In order to define a unique sign for any such fermionic many-particle wavefunction, we first decide on an ordering (that we subsequently stick to) of the states ν_i in the complete set of single-particle states. Then, when constructing the many-particle wavefunction out of N such states we use that ordering in the determinant. In this way we avoid ambiguities in the overall sign of the many-particle basis wavefunctions.

Second quantization

Let us now discuss basis states in second quantization. For concreteness we assume that the particles are fermions. As an example, consider a system of 3 fermions. Basis functions will then be specified in terms of 3 occupied single-particle states ν_1, ν_2, ν_3. Assuming that these are ordered in the way described in the previous paragraph (i.e. $\nu_1 < \nu_2 < \nu_3$), the basis function reads

$$\Phi(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \sum_{P \in S_3} \mathrm{sgn}(P) \phi_{\nu_1}(x_1) \phi_{\nu_2}(x_2) \phi_{\nu_3}(x_3). \tag{81}$$

Then the corresponding basis state in second quantization is given by

$$a^\dagger_{\nu_1} a^\dagger_{\nu_2} a^\dagger_{\nu_3} |0\rangle \tag{82}$$

where $a^\dagger_\nu$ creates a particle in the single-particle state ν and $|0\rangle$ is the vacuum state with no particles, defined by $a_\nu|0\rangle = 0$. This correspondence between basis states in first and second quantization generalizes in an obvious way to systems with a general number of particles N. Thus any basis state in first quantization has an analogous basis state in second quantization. There exists an explicit connection between the basis states in the two formalisms; this is discussed in the exercises for Week 13. In second quantization, a general fermionic basis state can be written on the form

$$(a^\dagger_1)^{n_1} (a^\dagger_2)^{n_2} (a^\dagger_3)^{n_3} (a^\dagger_4)^{n_4} \ldots |0\rangle \equiv |n_1, n_2, n_3, n_4, \ldots\rangle \tag{83}$$

where $n_\nu = 1$ if the single-particle state ν is occupied and $n_\nu = 0$ if it is empty (in this expression we have for simplicity labeled the single-particle states ν as integers 1,2,3,4,...). Note that on the left-hand side of (83) the creation operator $a^\dagger_\nu$ appears if and only if $n_\nu = 1$ (since $z^0 = 1$ and $z^1 = z$). The expression on the right-hand side is just a list of the occupation numbers in the ordered set of single-particle states. For this reason the second quantization formalism is often alternatively referred to as the occupation-number formalism.

The state (83) is an eigenstate of the number operator $\hat{n}_\nu = a^\dagger_\nu a_\nu$ with eigenvalue n_ν:

$$\hat{n}_\nu |n_1, n_2, n_3, n_4, \ldots\rangle = n_\nu |n_1, n_2, n_3, n_4, \ldots\rangle. \tag{84}$$

To prove this we use that

$$[\hat{n}_\nu, a^\dagger_{\nu'}] = a^\dagger_\nu \delta_{\nu,\nu'}. \tag{85}$$

There are two cases to consider: $n_\nu = 0$ and $n_\nu = 1$. If $n_\nu = 0$, $\hat{n}_\nu$ commutes with all the creation operators in $|n_1, n_2, n_3, n_4, \ldots\rangle$. Therefore we can move $\hat{n}_\nu$ past all creation operators until it stands to the immediate left of $|0\rangle$, and then we use $\hat{n}_\nu|0\rangle = 0$. If $n_\nu = 1$,

$\hat{n}_\nu$ commutes with all creation operators except $a_\nu^\dagger$. Thus we first move $\hat{n}_\nu$ past all creation operators that stand to the left of $a_\nu^\dagger$. Then we use $\hat{n}_\nu a_\nu^\dagger = a_\nu^\dagger \hat{n}_\nu + a_\nu^\dagger$. In the first term we can move $\hat{n}_\nu$ all the way to the right again and use $\hat{n}_\nu|0\rangle = 0$. The second term just gives $|n_1, n_2, n_3, n_4, \ldots\rangle$. So regardless of the value of n_ν we can write the result as the rhs of (84), which concludes the proof.

Second-quantized representation of single-particle operators

Consider an arbitrary single-particle operator in the first quantization formalism,

$$\hat{O} = \sum_{i=1}^{N} \hat{o}_i. \tag{86}$$

(It is called a single-particle operator because it is a sum of terms, each of which involves only a single particle.) Let $\{|\tilde{\alpha}\rangle\}$ denote the single-particle basis of eigenstates of $\hat{o}$, i.e.

$$\hat{o}|\tilde{\alpha}\rangle = o_{\tilde{\alpha}}|\tilde{\alpha}\rangle \tag{87}$$

where $o_{\tilde{\alpha}}$ is the eigenvalue of $\hat{o}$ associated with the eigenstate $|\tilde{\alpha}\rangle$. Then we claim that the representation of $\hat{O}$ in the second quantization formalism can be written

$$\hat{O} = \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} \hat{n}_{\tilde{\alpha}} \tag{88}$$

where $\hat{n}_{\tilde{\alpha}} = a_{\tilde{\alpha}}^\dagger a_{\tilde{\alpha}}$ is the number operator for state $|\tilde{\alpha}\rangle$. To prove this, we calculate the matrix elements of $\hat{O}$ in both first and second quantization and show that both formalisms give the same result (here, we use the many-particle basis that is built from the single-particle basis $\{|\tilde{\alpha}\rangle\}$). Consider then the matrix element $\langle\Phi'|\hat{O}|\Phi\rangle$ where $|\Phi\rangle$ and $|\Phi'\rangle$ are two arbitrary basis states in this many-particle basis set. Using second quantization this matrix element is

$$\begin{aligned}
\langle\Phi'|\hat{O}|\Phi\rangle &= \langle n'_{\tilde{\alpha}_1}, n'_{\tilde{\alpha}_2}, \ldots | \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} \hat{n}_{\tilde{\alpha}} | n_{\tilde{\alpha}_1}, n_{\tilde{\alpha}_2}, \ldots\rangle \\
&= \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} n_{\tilde{\alpha}} \langle n'_{\tilde{\alpha}_1}, n'_{\tilde{\alpha}_2}, \ldots | n_{\tilde{\alpha}_1}, n_{\tilde{\alpha}_2}, \ldots\rangle \\
&= \delta_{\Phi,\Phi'} \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} n_{\tilde{\alpha}}.
\end{aligned} \tag{89}$$

If we instead use first quantization we get the same result:

$$\begin{aligned}
\langle\Phi'|\hat{O}|\Phi\rangle &= \int d^N x \; \Phi'^*(x_1, \ldots, x_N) \sum_{i=1}^{N} \hat{o}(x_i) \Phi(x_1, \ldots, x_N) \\
&= \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} n_{\tilde{\alpha}} \int d^N x \; \Phi'^*(x_1, \ldots, x_N) \Phi(x_1, \ldots, x_N) \\
&= \delta_{\Phi,\Phi'} \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} n_{\tilde{\alpha}},
\end{aligned} \tag{90}$$

where we used a result shown in Exercise 1(iii) for Week 13. This proves (88). Note again that in (88) the single-particle basis used is the one that diagonalizes $\hat{o}$, i.e. this expression for $\hat{O}$ is not valid for an arbitrary basis. However, starting from this expression we can use the basis transformations considered earlier to derive an expression for $\hat{O}$ that *is* valid in an arbitrary basis:

$$\begin{aligned}\hat{O} &= \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} a^\dagger_{\tilde{\alpha}} a_{\tilde{\alpha}} = \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} \left(\sum_{\alpha} \langle \alpha | \tilde{\alpha} \rangle a^\dagger_\alpha \right) \left(\sum_{\beta} \langle \tilde{\alpha} | \beta \rangle a_\beta \right) \\ &= \sum_{\alpha,\beta} \langle \alpha | \underbrace{\left(\sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle o_{\tilde{\alpha}} \langle \tilde{\alpha}| \right)}_{\hat{o}} |\beta\rangle a^\dagger_\alpha a_\beta = \sum_{\alpha,\beta} \langle \alpha | \hat{o} | \beta \rangle a^\dagger_\alpha a_\beta. \end{aligned} \tag{91}$$

Here we used that the eigenvalue equation $\hat{o}|\tilde{\alpha}\rangle = o_{\tilde{\alpha}}|\tilde{\alpha}\rangle$ implies that we can write $\hat{o} = \hat{o}I = \hat{o}\sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle\langle\tilde{\alpha}| = \sum_{\tilde{\alpha}} o_{\tilde{\alpha}} |\tilde{\alpha}\rangle\langle\tilde{\alpha}| = \sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle o_{\tilde{\alpha}} \langle\tilde{\alpha}|$. The matrix element $\langle \alpha | \hat{o} | \beta \rangle$ can be written[3]

$$\langle \alpha | \hat{o} | \beta \rangle = \int dx \int dx' \, \langle \alpha | x \rangle \underbrace{\langle x | \hat{o} | x' \rangle}_{\hat{o}(x)\delta(x-x')} \langle x' | \beta \rangle = \int dx \, \langle \alpha | x \rangle \hat{o}(x) \langle x | \beta \rangle = \int dx \, \phi^*_\alpha(x) \hat{o}(x) \phi_\beta(x). \tag{92}$$

Thus the second quantized representation of a single-particle operator $\hat{O}$ can be written

$$\hat{O} = \sum_{\alpha,\beta} \left[\int dx \, \phi^*_\alpha(x) \hat{o}(x) \phi_\beta(x) \right] a^\dagger_\alpha a_\beta. \tag{93}$$

In particular, using Eqs. (64)-(65) this can be expressed in terms of field operators as

$$\hat{O} = \int dx \, \psi^\dagger(x) \hat{o}(x) \psi(x). \tag{94}$$

Using Eqs. (88), (93), or (94) it is now easy to (re-)derive the second-quantized representations of various single-particle operators from their first-quantized form. Let's start with the kinetic energy operator (27). Eq. (22) follows directly from (88) by noting that the electronic eigenfunctions of $-(\hbar^2/2m)\nabla^2$ have quantum numbers $(\boldsymbol{k}, \sigma)$ where $\boldsymbol{k}$ labels the plane wave with associated eigenvalue $\hbar^2\boldsymbol{k}^2/2m$. Similarly, Eq. (23) follows immediately from (94) with $\hat{o}(x) = -(\hbar^2/2m)\nabla^2$. By exactly the same reasoning, the total momentum operator $\boldsymbol{P}$, which in first-quantization is given by

$$\boldsymbol{P} = \sum_{j=1}^{N} \frac{\hbar}{i} \nabla_j, \tag{95}$$

[3]Note that $\langle x|\hat{o}|x'\rangle = \hat{o}(x)\delta(x-x')$ is valid also if $\hat{o}$ is not diagonal in the x-basis, for example if $\hat{o}$ is the momentum operator $\hat{p}$ or some power of it. To see this, let's forget about spin for simplicity and take x to mean position only. Then from $[\hat{x},\hat{p}] = i\hbar$ we get $\langle x||[\hat{x},\hat{p}]||x'\rangle = i\hbar\delta(x-x')$. On the other hand, $\langle x|[\hat{x},\hat{p}]|x'\rangle = \langle x|(\hat{x}\hat{p}-\hat{p}\hat{x})|x'\rangle = (x-x')\langle x|\hat{p}|x'\rangle$. Therefore $\langle x|\hat{p}|x'\rangle = i\hbar\delta(x-x')/(x-x')$. Now use $(d/dx)\delta(x-x') = (du/dx)(d/du)\delta(u)$ with $u = x-x'$. Using $(d/du)\delta(u) = -\delta(u)/u$ this gives $(d/dx)\delta(x-x') = -\delta(x-x')/(x-x')$. Thus $\langle x|\hat{p}|x'\rangle = -i\hbar(d/dx)\delta(x-x')$ which is on the claimed form with $\hat{p}(x) = -i\hbar(d/dx)$.

can in second quantization be written

$$\boldsymbol{P} = \sum_{\boldsymbol{k}\sigma} \hbar \boldsymbol{k}\; a^\dagger_{\boldsymbol{k}\sigma} a_{\boldsymbol{k}\sigma} = \sum_\sigma \int d^3r\; \psi^\dagger_\sigma(\boldsymbol{r}) \frac{\hbar}{i} \nabla \psi_\sigma(\boldsymbol{r}). \tag{96}$$

Let us derive the first expression here using (93) to illustrate its use as well. With $x = (\boldsymbol{r}, s)$ and $\beta = (\boldsymbol{k}, \sigma)$ the eigenfunctions in (93) are of the form $\phi_\beta(x) = \phi_{\boldsymbol{k}\sigma}(\boldsymbol{r}, s) = (1/\sqrt{V}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \delta_{s\sigma}$. Thus

$$\begin{aligned}
\int dx\; \phi^*_\alpha(x) \frac{\hbar}{i} \nabla \phi_\beta(x) &= \sum_s \int_V d^3r \left(\frac{1}{\sqrt{V}} e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}} \delta_{s\sigma'} \right) \frac{\hbar}{i} \nabla \left(\frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \delta_{s\sigma} \right) \qquad (97) \\
&= \sum_s \int_V d^3r \left(\frac{1}{\sqrt{V}} e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}} \delta_{s\sigma'} \right) \frac{\hbar}{i} i\boldsymbol{k} \left(\frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \delta_{s\sigma} \right) \\
&= \hbar \boldsymbol{k} \left(\frac{1}{V} \int d^3r\, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}} \right) \left(\sum_s \delta_{s\sigma'} \delta_{s\sigma} \right) \\
&= \hbar \boldsymbol{k}\; \delta_{\boldsymbol{k}\boldsymbol{k}'} \delta_{\sigma\sigma'}. \qquad (98)
\end{aligned}$$

Putting this back into (93) we get the first expression in (96). Finally, let us consider the density operator $\rho(x)$, whose first-quantized form is given in (32). Eq. (93) gives

$$\begin{aligned}
\rho(x) &= \sum_{\alpha\beta} \left(\int dy\; \phi^*_\alpha(y) \delta(x-y) \phi_\beta(y) \right) a^\dagger_\alpha a_\beta \\
&= \sum_{\alpha,\beta} \phi^*_\alpha(x) \phi_\beta(x)\; a^\dagger_\alpha a_\beta. \qquad (99)
\end{aligned}$$

where the single-particle basis $\{|\alpha\rangle\}$ is arbitrary. Note that we used y as an integration variable in the integral here, since x was already "taken" since $\rho(x)$ depends on x as a parameter. Using (64)-(65) we immediately get (31). A more direct route to (31) would be to use (94):

$$\rho(x) = \int dy\; \psi^\dagger(y) \delta(x-y) \psi(y) = \psi^\dagger(x) \psi(x). \tag{100}$$

What about two-particle operators? The method of calculating matrix elements in both first and second quantization and demanding that they be identical, could also be used to derive the second-quantized representation (40) of two-particle operators. However, this proof is much more tedious than the one we gave earlier (Eqs. (29)-(40)) and won't be presented here.