# 1

# Second quantization

### Summary

"First quantization" leads to the Schrodinger equation for the wavefunction in which the classical hamiltonian is an operator with the momentum $\mathbf{p}$ replaced by $-i\hbar\,\boldsymbol{\nabla}$. The wavefunction is a single-particle function $\psi$ or a many-particle function $\Psi$ for a fixed number of particles that evolves in time an carries all the information about the state of the system. In "Second Quantization" the expectation value of the hamiltonian with a quantum wavefunction for one particle (for one-body terms) or two particles (for two-body interaction terms) is "quantized again", writing it as an operator that applies for any number of particles. The creation and annihilation operators obey commutation or anticommutation rules the enforce the proper symmetries. This is of great value in dealing with the myriad terms that appear in perturbation theory expansions for interacting-particle systems.

## 1.1 First quantization

"First quantization" denotes the transition from classical to quantum mechanics in which the classical hamiltonian $H(\{\mathbf{r}_i\}, \{\mathbf{r}_i\})$ and equations of motion for a system of particles $i = 1, \dots, N$ becomes the operator in the time-dependent Schrödinger equation $i\hbar\frac{d}{dt}\Psi = \hat{H}\Psi$. The hamiltonian operator $\hat{H}$ is the classical $H$ with the momentum $\mathbf{p}_i$ replaced by $-i\hbar\,\boldsymbol{\nabla}_i$. All information on the quantum $N$-particle system as it evolves in time is contained in the time-dependent wavefunction $\Psi(\{\mathbf{r}_i\}, t)$. Any observable can be expressed as an expectation value $\langle\Psi(\{\mathbf{r}_i\}, t)|\hat{O}|\Psi(\{\mathbf{r}_i\}, t)\rangle$ of time-independent operators $\hat{O}$.

First quantization is the most useful form for quantitative solutions of the Schrödinger equation in cases where the particle number is fixed. This is the form used in 1 for one-body and independent-particle methods in quantum theory. The independent-particle states $\psi(\mathbf{r})$ can be calculated directly from the differential form of the Schrödinger equation. In cases where the particle number is not fixed, it is a simple matter of the Fermi-Dirac function to specify the average occupation of the independent-particle states.

First quantization is also the most useful formulation in many approaches that treat the full interacting many-body problem. In particular, the quantum Monte Carlo methods are cast in terms of solving the Schrödinger equation for a fixed number of particles - a differential equation in $3N + 1$ dimensions if there are three space dimensions plus time. A great advantage is that the solution can be found in continuous space without any approximations due to the introduction of a finite basis set. Similarly the Coulomb interaction that diverges at short distance can be treated with no approximation, and no need for a short-range cutoff that would be inherent in a finite basis.

## 1.2 Second quantization

"Second quantization" reformulates the equations of quantum mechanics in a way that greatly facilitates the application of the theory to many interacting particles. The concepts are essential in relativistic quantum mechanics[2, 3, 4], where creation and annihilation of particles are intrinsic to the theory, and they are extremely fruitful in non-relativistic theory[5, 6, 7, 8, 9, 4] of interacting many-body systems. The formalism is especially fruitful for description of Green's functions and response functions in terms of addition and removal of particles from the system, which is the basis for much of the developments in the remainder of the course. The ideas can be cast in terms of occupation number representation for indistinguishable particles, with creation and annihilation operators that change the number of particles. Alternatively second quantization can be formulated elegantly in terms of field operators in which the wavefunctions of first-quantized theory become operators that generate the quantum system from the vacuum.

### Occupation number representation

States for many indistinguishable particles can be specified in terms of a basis of independent particles states, which in the first-quantized form are independent-particle functions $\psi_i$, $i = 1, \ldots, M$, where $M$ denotes the maximum number of independent-particle functions considered. Formally we can let $M \to \infty$ for a complete set of states. A basis for many-particle states can be formed from products of the $\psi_i$ with proper accounting of the fact that the wavefunctions must be symmetric for bosons and antisymmetric for fermions. The states can be written as $|n_1, n_2, n_3, \ldots, n_k, \ldots, n_M\rangle$, which denotes a state with $\sum_i n_i = N$ particles. The full space of states for the many-body system can then be expressed as as the set many-particle states with all possible numbers of particles $N$. Of course, these are not the exact states for many interacting particles, but this defines basis in which the full many-body problem can be expressed.

**Bosons** The wavefunction for indistinguishable bosons must be symmetric under exchange of any two particles. This property follows if one defines time-independent creation and annihilation operators $b^\dagger$ and $b$ that satisfy the relations

$$[b_k, b_{k'}^\dagger] = \delta_{k,k'}$$
$$[b_k, b_{k'}] = [b_k^\dagger, b_{k'}^\dagger] = 0 \tag{1.1}$$

where $[a, b] = ab - ba$. This leads to all the properties of bosons, in particular,

$$b_k|n_1, \ldots, n_k, \ldots\rangle = \sqrt{n_k}\,|n_1, \ldots, n_k - 1, \ldots\rangle$$
$$b_k^\dagger|n_1, \ldots, n_k, \ldots\rangle = \sqrt{n_k + 1}|n_1, \ldots, n_k + 1, \ldots\rangle \tag{1.2}$$

Any given state can be generated from the vacuum state $|0\rangle \equiv |0, \ldots, n_k = 0, \ldots\rangle$ by application of the creation operators

$$|n_1, \ldots, n_k, \ldots\rangle \; = \; \ldots (b_k^\dagger)^{n_k} \ldots (b_1^\dagger)^{n_1}|0\rangle \tag{1.3}$$

and the number operator for state $k$ is

$$b_k^\dagger \, b_k |n_1, \ldots, n_k, \ldots\rangle \; = \; |n_1, \ldots, n_k, \ldots\rangle, \;\; n_k = 0, 1, 2, \ldots, \infty \tag{1.4}$$

**Fermions** The properties of indistinguishable fermions follow from creation and annihilation operators $c^\dagger$ and $c$ that obey the relations

$$\{c_k, c_{k'}^\dagger\} = \delta_{k,k'}$$
$$\{c_k, c_{k'}\} = \{c_k^\dagger, c_{k'}^\dagger\} = 0 \tag{1.5}$$

where $\{a, b\} = ab - ba$ is the anticommutator. In particular, it follows from the second line of Eq. 1.5 that two fermions cannot be in the same state; the occupation of any state $k$ can only be $n_k = 0$ or $n_k = 1$. The application of the operators is analogous to Eq. 1.2; however, the states must be defined with a specified order of the single-particle states with a change of sign whenever any two creation or two annihilation operators are interchanged. From these relations it follows that (some authors include $\sqrt{n_k}$ and $\sqrt{n_k - 1}$ factors similar to the the boson expressions)

$$c_k|n_1, \ldots, n_k, \ldots\rangle \; = \; \begin{cases} (-1)^{S_k} |n_1, \ldots, n_k - 1, \ldots\rangle, & n_k = 1, \\ 0, & n_k = 0 \end{cases}$$

$$c_k^\dagger|n_1, \ldots, n_k, \ldots\rangle \; = \; \begin{cases} (-1)^{S_k} |n_1, \ldots, n_k + 1, \ldots\rangle, & n_k = 0, \\ 0, & n_k = 1 \end{cases}$$

where the sign factor $(-1)^{S_k}$ with $S_k = \sum_{k'=1}^{k'=k-1} n_{k'}$ takes into account the change of sign each time the operators are exchanged. A state can be generated from the vacuum state $|0\rangle$ by application of the creation operators in the specified order (reading from right to left)

$$|n_1, \ldots, n_k, \ldots\rangle \; = \; \ldots (c_k^\dagger)^{n_k} \ldots (c_1^\dagger)^{n_1}|0\rangle, \tag{1.6}$$

where $n_k = 1$ or $n_k = 0$. The number operator has the same as for bosons

$$c_k^\dagger \, c_k |n_1, \ldots, n_k, \ldots\rangle \; = \; n_k \, |n_1, \ldots, n_k, \ldots\rangle, \quad n_k = 0, 1. \tag{1.7}$$

### One- and two-particle operators

Expressions for operators in second quantized form can be derived from the fact that it must yield the same result as the first quantized form in a state with a given particle number. Consider single-particle operator $\hat{O} \equiv \sum_i O(\mathbf{r}_i)$ where $i$ denotes the particles. The expectation value in a state $\psi(\mathbf{r})$ with one particle is

$$\langle\psi|\hat{O}|\psi\rangle = \int d\mathbf{r}\psi^*(\mathbf{r})O(\mathbf{r})\psi(\mathbf{r}) \tag{1.8}$$

If we let $a^\dagger$ and $a$ denote creation and annihilation operators for either bosons or fermions, we can expand $\psi$ in the single-particle eigenstates $\psi_k(\mathbf{r})$,

$$\psi(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) a_k^\dagger |0\rangle. \tag{1.9}$$

It follows that the operator $\hat{O}$ expressed in terms of the second-quantized operators as

$$\hat{O} = \sum_{k_1,k_2} a_{k_1}^\dagger O_{k_1,k_2} a_{k_2}, \quad O_{k_1,k_2} = \int d\mathbf{r}\, \psi_{k_1}^*(\mathbf{r}) O(\mathbf{r}) \psi_{k_2}(\mathbf{r}). \tag{1.10}$$

Similarly a two-particle interaction term $\frac{1}{2}\sum_{i,j} V(|\mathbf{r}_i - \mathbf{r}_j|)$ can be expressed as

$$\hat{V} = \sum_{k_1,k_2,k_3,k_4} a_{k_1}^\dagger a_{k_2}^\dagger V_{k_1,k_2,k_3,k_4} a_{k_3} a_{k_4}, \quad V_{k_1,k_2,k_3,k_4} = \int d\mathbf{r}\, \psi_{k_1}^*(\mathbf{r}) \psi_{k_2}^*(\mathbf{r}') V(|\mathbf{r}-\mathbf{r}'|) \psi_{k_3}^*(\mathbf{r}') \psi_{k_4}(\mathbf{r}). \tag{1.11}$$

Note the order of the operators with destruction operators to the right; this is essential for all terms to have zero expectation in the vacuum state. The advantage of this representation is that it applies for both bosons and fermions and for any number of particles; the symmetry of the particles is accounted for the by the (anti)commutation rules for the operators.

### Fields

In order to escape from the from the dependence upon the choice of a basis, a more elegant form can be introduced in terms of field operators. Here we consider fermions; a different variation is needed for bosons. In analogy to Eq. 1.9 define

$$\hat{\psi}(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) c_k$$
$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_k \psi_k(\mathbf{r}) c_k^\dagger \tag{1.12}$$

and assume the sum is over a complete set of single-particle quantum numbers. It follows from the definition of the creation and annihilation operators for fermions that $\hat{\psi}$ and $\hat{\psi}^\dagger$ obey the relations

$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} = \delta(\mathbf{r}-\mathbf{r}')$$
$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} = \{\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}')\} = 0$$
$$n(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}). \tag{1.13}$$

This suffices to express the interacting-electron hamiltonian. The general form is $\hat{H} = \hat{H}_0 + \hat{H}_{int}$, where $\hat{H}_0$ is a sum of one particle terms and $\hat{H}_{int}$ is the two-body interaction. Then the hamiltonian in second quantized form can be written

$$\hat{H} = \int d\mathbf{r}\, \hat{\psi}^\dagger(\mathbf{r}) \hat{H}_0(\mathbf{r}) \hat{\psi}(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}'\, \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \hat{H}_{int}(\mathbf{r},\mathbf{r}') \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}). \tag{1.14}$$

### 1.3 Jellium

Jellium is the simplest example of condensed matter. Since the background is homogeneous, it is most convenient to work in a basis of plane waves. Then the hamiltonian can be written

$$\hat{H} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \frac{1}{2}\sum_{\mathbf{q}} V_q \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} c_{\mathbf{k}+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}'-\mathbf{q}\sigma'}^\dagger c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma}$$

$$= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \frac{1}{2}\sum_{\mathbf{q}} V_q (\hat{\rho}_{-\mathbf{q}}\hat{\rho}_{k\mathbf{q}} - N), \tag{1.15}$$

where $V_k q = \frac{1}{\Omega}\frac{4\pi e^2}{q^2}$ and $\hat{\rho}_{\mathbf{k}} = \sum_{\mathbf{k}\sigma} c_{\mathbf{k}+\mathbf{q}\sigma}^\dagger c_{\mathbf{k}\sigma}$. In general one always has sums of the form $\frac{1}{\Omega}\sum_{\mathbf{k}} \to \frac{1}{(2\pi)^D}\int d^D\mathbf{k}$, where $D$ is the dimension.

References: Second quantization: Mahan 1.1,1.2,1.3A, Pines p. 18, p. 67; Fetter; other texts; Hamiltonian Mahan, ch 1.2, Pines Ch 3; Correlation functions: class notes, Pines, Ch. 3. (We will sometimes set the normalization volume $\Omega = 1$ following Pines).

This hamiltonian is valid only for homogeneous Jellium because we have assumed the single particle terms are diagonal in momentum index $p$. However, a general form can be made for for atoms, crystals, and molecules if one changes only the single particle part, since the electron-electron interactions always have the Coulombic form shown.

For example, the exchange energy can be derived as (Pines, p 68-69)

$$E_x = \frac{1}{2}\sum_k V_k \sum_{p\sigma p'\sigma'} \langle 0|c_{p+k\sigma}^+ c_{p'-k\sigma'}^+ c_{p'\sigma'} c_{p\sigma}|0\rangle$$

$$= -\frac{1}{N}\left(-\frac{1}{2}\right)\sum_{k,k',\sigma} V_{k'}\langle \rho_{k+k',\sigma}\rho_{k,\sigma}\rangle$$

$$= \frac{1}{N}\left(-\frac{1}{2}\right)\sum_{k,k'<k_F} V_{k-k'} = -\frac{0.916}{r_s}\ Ryd. \tag{1.16}$$

**Hartree-Fock Theory for Jellium**

We have previously derived the form of exchange in the first-quantized notation. The key ingredients were the pair distribution function defined by

$$g(r,r') = \frac{1}{\rho(r)}\frac{1}{\rho(r')}p(r,r') \tag{1.17}$$

where

$$p(r,r') = \langle\Psi|\sum_{i\neq j}\delta(r-r_i)\delta(r-r_j)|\Psi\rangle \tag{1.18}$$

is the joint probability of simultaneously finding an electron at points $r$ and $r'$.

In second quantized form in terms of the elementary excitations (plane waves) it is most convenient to work in k-space. For a homogeneous system one can define the static structure factor $S(k)$ (see Pines and Fulde)

$$S(k) = \int d^3 r p(r) exp(ikr) \tag{1.19}$$

$$= \frac{1}{N} \langle \Psi | \sum_{i,j} exp(-ik(r_i - r_j)) | \Psi \rangle \tag{1.20}$$

$$= \frac{1}{N} \langle \Psi | \rho_{-k} \rho_k | \Psi \rangle \tag{1.21}$$

which includes the self-term. In terms of creation and annihilation operators, this may be written

$$S(k) = \frac{1}{N} \langle 0 | \sum_{p\sigma} c^\dagger_{p-k\sigma} c_{p\sigma} \sum_{p'\sigma'} c^\dagger_{p'+k\sigma'} c_{p'\sigma'} | 0 \rangle, \tag{1.22}$$

which after some algebra can be shown to be

$$S(k) = N\delta_{k=0} + \frac{1}{N} \sum_{p\sigma} (1 - n_{p-k\sigma}) n_{p\sigma}, \tag{1.23}$$

where is the occupation $n_{p\sigma} = 1$ for $k < k_F$ and 0 for $k > k_F$. (See Pines p 75 and class notes.)

Thus the Hartree-Fock structure factor is very simple in k space (See Pines p 75 and class notes.) For $k \neq 0$, define $x = \frac{k}{2k_F}$, in which case

$$S(k) = \frac{3}{2}x - \frac{1}{2}x^3, x < 1 \tag{1.24}$$

$$S(k) = 1, x > 1 \tag{1.25}$$

A main point is that $S(k) = 1$ for $k > 2k_F$, so that the the particles are uncorrelated except for the Pauli exclusion between states with $k < k_F$.

For a homogeneous system, one can Fourier transform this expression

$$g(r) = \frac{1}{N} \sum_k (S(k) - 1) exp(ikr) \tag{1.26}$$

to recover the same results as derived before for the exchange hole in real space. (Note: For an uncorrelated system $S(k) = 1$, $k \neq 0$, and $S(0) = N$, (self term). Some texts define $S$ without the self term, so that $S(0) = 0$, e.g., Mahan, p. 74.)

**Beyond Hartree-Fock: Correlations**
In the class notes we give the main reasons why it is difficult to go beyond H-F. In finite systems, one finds the configuration-interaction expansion which grows exponentially with the number of particles. In condensed matter expansions formally diverge (Gellmann-Bruckner). This is easily seen in Jellium just by examining the integrals. What to do? This is the subject of the many-body theory of the course.

## FURTHER READING

Fetter, A. L. and J. D. Walecka*Quantum Theory of Many-particle Systems* (McGraw-Hill Book Company, New York, 1971). Many-particle Systems" (McGraw-Hill Book Company, New York, 1971), (Reprinted in paperback by Dover) This book presents quantum field theory in careful detail. The notation is followed here and the reader is referred to this text for more complete discussion.

Feynman, R. P. *Statistical Mechanics: A set of lectures* (The Benjamin/Cummings Publishing Company, Reading, Massachusetts, 1970.) (paperback) Basic principles preented with great insight and with explicit details for simple examples.

Ziman, J. M. *Elements of Advanced Quantum Theory* (Cambridge University Press, 1969). (paperback) Readable description of second quantization with simple examples - sometimes with equations that are oversimplified to avoid details.

Mahan, G. D. *Many-Particle Physics, 3rd Ed.* (Kluwer Academic/Plenum Publishers, New York, 2000). Compendium of problems in many-body physics.

Pines, D., "Elementary Excitations in Solids" ( Wiley, New York, 1964) (paperback). Somewhat old fashioned but excellent presentation of ideas and physical reasoning.

## Exercises

1.1 Exercise