FIP10601 – Text 10

Electronic Hamiltonian in second quantization

When discussing the Hartree and Hartree-Fock approximations as well as DFT, we used wavefunctions that depended on coordinates of all the electrons in the system. Since solids are macroscopic, such wave functions, in general, cannot be determined. Even in the independent-electron approximation the system wavefunctions would be Slater determinants of dimension equal to the number of electrons. So, it is convenient to avoid the coordinate representation, which is done in the usual formalism of many-body theory, as will be seen in the following.

Occupation number representation

Although Slater determinants are not solutions of the interacting-electron problem, they provide a basis for a useful representation. In such a basis, the noninteracting part of the Hamiltonian is diagonal. We will use this basis to rewrite the complete Hamiltonian, but in doing so we will avoid to work explicitly with functions of coordinates.

Taking into account that the single-particle states are known (Bloch states for a given lattice potential), we just need to specify which ones take part in a given Slater determinant. We refer to them as individual states *occupied* by electrons in the corresponding basis state of the system. The individual states are characterized by a wavevector $\mathbf{k}$ and a spin quantum number σ, being denoted by $|\mathbf{k}\sigma\rangle$ in the (abstract) one-electron Hilbert space. In coordinate/spin representation, we have $\langle \mathbf{r}|\mathbf{k}\sigma\rangle = \psi_{\mathbf{k}}(\mathbf{r})\chi_\sigma$, which can be generalized to include a band index (for simplicity, we will restrict this discussion to a single band). The basis vectors of an abstract space containing **states of arbitrary electron number**, known as *Fock space*, may be represented as

$$|n_{\mathbf{k}_1\sigma_1}\, n_{\mathbf{k}_2\sigma_2}\, n_{\mathbf{k}_3\sigma_3}\, \ldots\rangle\ , \tag{1}$$

where $n_{\mathbf{k}\sigma}$ is the *occupation number* of the state $|\mathbf{k}\sigma\rangle$, i.e., the number of electrons in this individual state. Due to the fermionic nature of electrons, this number can only assume the values 0 (zero) or 1 (one).

It is important to point out that, by construction, there is a **one-to-one correspondence** between a particular basis vector of the Fock space and a Slater determinant built with the individual Bloch states $|\mathbf{k}_i\sigma_i\rangle$ for which $n_{\mathbf{k}_i\sigma_i} = 1$.

Second-quantization formalism

The Fock space contains states with any number of particles. Physical states of a system of N electrons are vectors belonging to an N-particle subspace, i.e., spanned by basis vectors containing N occupation numbers equal to 1 and all the others equal to zero. As we will see, it is convenient to define operators that allow us to move between subspaces with different particle numbers. Such operators (for obvious reasons) are called single-particle *creation* and *annihilation* operators. We can view a general N-particle state as being obtained from the *vacuum* (zero-particle state) by successive application of N creation operators.

For simplicity of notation, we begin by considering a generic system of fermions, denoting by a single Greek letter the set of quantum numbers that identifies a single-particle state. Denoting by $c_\alpha^\dagger$ the creation operator of a fermion in the single-particle state $|\alpha\rangle$, we have, for a generic basis state in Fock space,

$$|n_\alpha\, n_\beta\, n_\gamma\, \ldots\rangle = (c_\alpha^\dagger)^{n_\alpha}(c_\beta^\dagger)^{n_\beta}(c_\gamma^\dagger)^{n_\gamma}\ldots|0\rangle\ , \tag{2}$$

where $|0\rangle \equiv |000\ldots\rangle$ is a simplified notation for the vacuum, and the n's can assume the values 0 or 1.

The **order** of creation operators in Eq. (2) is relevant. This can be checked using the correspondence with Slater determinants. Each subscript is associated with a row of the determinant. So, an exchange of two creation operators corresponds to an exchange of two rows of the determinant, with a consequent sign change. We say, then, that two creation operators *anticommute*, which means that their *anticommutator* is null:

$$\{c_\alpha^\dagger, c_\beta^\dagger\} \equiv c_\alpha^\dagger c_\beta^\dagger + c_\beta^\dagger c_\alpha^\dagger = 0\ . \tag{3}$$

An immediate consequence of this relationship is that $\left(c_\alpha^\dagger\right)^2 = 0$, expressing Pauli's Exclusion Principle.

Considering the **dual** Fock space, i.e., the *bra*'s corresponding to the *ket*'s of Eq. (2), we see that c_α, the Hermitian conjugate of $c_\alpha^\dagger$, plays the role of creation operator on the *bra*-space. Then, the structure of bra-ket scalar products allows to realize that $c_\alpha^\dagger$ annihilates on *bra*'s while c_α annihilates on *ket*'s. The usage is to refer to the operators as creation or anihilation based on their actions on the ket-space. Thus, $c_\alpha^\dagger$ is called a creation operator, and c_α is an annihilation operator. From Eq. (3) and the conjugation relationship between c_α and $c_\alpha^\dagger$ we have the anticommutation relation for annihilation operators,

$$\{c_\alpha, c_\beta\} \equiv c_\alpha c_\beta + c_\beta c_\alpha = 0\ , \tag{4}$$

also showing that $c_\alpha^2 = 0$, as should be expected. The algebra of fermion operators is completed by the relation

$$\{c_\alpha, c_\beta^\dagger\} = \delta_{\alpha\beta}\ , \tag{5}$$

which can be easily verified by inspecting a generic Fock-space matrix element of this anticommutator.

From the above analysis of the generic algebra of *fermion operators*, we conclude that the complete set of anticommutation relations between creation and annihilation operators of electrons in Bloch states (with specified spin) is

$$\{c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma'}\} = 0 \,, \quad \{c^\dagger_{\mathbf{k}\sigma}, c^\dagger_{\mathbf{k}'\sigma'}\} = 0 \,, \quad \{c_{\mathbf{k}\sigma}, c^\dagger_{\mathbf{k}'\sigma'}\} = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'} \,. \tag{6}$$

As we will see in more detail below, any physically relevant operator in this formalism can be written in terms of creation and/or annihilation operators. A particularly useful one is the *occupation-number operator*, defined as

$$\hat{n}_{\mathbf{k}\sigma} \equiv c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \,. \tag{7}$$

with a *hat* added to avoid confusion with its eigenvalues. It is easy to check that these eigenvalues are 0 and 1, the only possible occupation numbers of a single-fermion state.

The following **commutation** relations involving the occupation-number operator might be useful:

$$[\hat{n}_{\mathbf{k}\sigma}, c^\dagger_{\mathbf{k}\sigma}] = c^\dagger_{\mathbf{k}\sigma} \,, \tag{8}$$

$$[\hat{n}_{\mathbf{k}\sigma}, c_{\mathbf{k}\sigma}] = -c_{\mathbf{k}\sigma} \,. \tag{9}$$

We usually deal with systems in which the number of particles is conserved. So, the relevance of operators that change this number it is not obvious. Their usefulness will be put into evidence in what follows.

Operator representation in Fock space

It is convenient to express **any** operator in terms of creation and annihilation operators, since we know their action on Fock-space vectors. We begin by noticing that a product like $c^\dagger_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma}$, which conserves the number of particles, has the same effect of a **projector** in the Hilbert space. For instance, the result of applying this product to any state of a single electron is equivalent to the result of applying the projector $|\mathbf{k}'\sigma'\rangle\langle\mathbf{k}\sigma|$ to the corresponding Hilbert-space state written as a linear combination of Bloch states.

So, given that a generic single-particle operator $A^{(1)}$ may be written as

$$A^{(1)} = \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} |\mathbf{k}'\sigma'\rangle\langle\mathbf{k}'\sigma'|A^{(1)}|\mathbf{k}\sigma\rangle\langle\mathbf{k}\sigma| \equiv \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} A^{(1)}_{\mathbf{k}'\sigma',\mathbf{k}\sigma} |\mathbf{k}'\sigma'\rangle\langle\mathbf{k}\sigma| \,, \tag{10}$$

we can represent it in the form

$$A^{(1)} = \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} A^{(1)}_{\mathbf{k}'\sigma',\mathbf{k}\sigma}\, c^\dagger_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} \,. \tag{11}$$

Note that, with the same physical meaning for $A^{(1)}$, Eq. (10) refers to a single-electron Hilbert space while Eq. (11) defines an operator in the Fock space.

For operators that do not depend on spin, Eq. (11) simplifies to

$$A^{(1)} = \sum_{\mathbf{k}\mathbf{k}'\sigma} A^{(1)}_{\mathbf{k}'\mathbf{k}}\, c^\dagger_{\mathbf{k}'\sigma} c_{\mathbf{k}\sigma} \ . \tag{12}$$

The matrix elements can be evaluated in coordinate representation:

$$A^{(1)}_{\mathbf{k}'\mathbf{k}} = \int \mathrm{d}^3 r\, \psi^*_{\mathbf{k}'}(\mathbf{r}) A^{(1)} \psi_{\mathbf{k}}(\mathbf{r}) \ . \tag{13}$$

Similarly, let us consider a generic two-particle operator $B^{(2)}$ (also spin-independent, for simplicity). The projectors now involve two-particle states, written as direct products of single-particle ones, and the development is similar:

$$\begin{aligned} B^{(2)} &= \sum_{\mathbf{k}_1\mathbf{k}'_1\sigma_1} \sum_{\mathbf{k}_2\mathbf{k}'_2\sigma_2} |\mathbf{k}'_1\sigma_1\rangle|\mathbf{k}'_2\sigma_2\rangle \, \langle \mathbf{k}'_1\sigma_1|\langle \mathbf{k}'_2\sigma_2|B^{(2)}|\mathbf{k}_2\sigma_2\rangle|\mathbf{k}_1\sigma_1\rangle \, \langle \mathbf{k}_2\sigma_2|\langle \mathbf{k}_1\sigma_1| \\ &= \sum_{\mathbf{k}_1\mathbf{k}'_1\sigma_1} \sum_{\mathbf{k}_2\mathbf{k}'_2\sigma_2} B^{(2)}_{\mathbf{k}'_1\mathbf{k}'_2,\mathbf{k}_2\mathbf{k}_1} \, |\mathbf{k}'_1\sigma_1\rangle|\mathbf{k}'_2\sigma_2\rangle\langle \mathbf{k}_2\sigma_2|\langle \mathbf{k}_1\sigma_1| \ , \end{aligned} \tag{14}$$

with

$$B^{(2)}_{\mathbf{k}'_1\mathbf{k}'_2,\mathbf{k}_2\mathbf{k}_1} = \int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, \psi^*_{\mathbf{k}'_1}(\mathbf{r}) \psi^*_{\mathbf{k}'_2}(\mathbf{r}') B^{(2)} \psi_{\mathbf{k}_2}(\mathbf{r}') \psi_{\mathbf{k}_1}(\mathbf{r}) \ . \tag{15}$$

Comparing with the one-particle case, we see that a projector in a two-particle space is equivalent to the action of two annihilation and two creation operators. Thus, the Fock-space representation of the operator $B^{(2)}$ is

$$B^{(2)} = \sum_{\mathbf{k}_1\mathbf{k}'_1\sigma_1} \sum_{\mathbf{k}_2\mathbf{k}'_2\sigma_2} B^{(2)}_{\mathbf{k}'_1\mathbf{k}'_2,\mathbf{k}_2\mathbf{k}_1} c^\dagger_{\mathbf{k}'_1\sigma_1} c^\dagger_{\mathbf{k}'_2\sigma_2} c_{\mathbf{k}_2\sigma_2} c_{\mathbf{k}_1\sigma_1} \ . \tag{16}$$

Electronic Hamiltonian

The general rules derived above to express one- and two-particle operators in Fock space allow to rewrite the electronic Hamiltonian [Eq. (1) of Text 9] in the form

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}}\, c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \tfrac{1}{2} \sum_{\substack{\mathbf{k}_1\mathbf{k}'_1\sigma \\ \mathbf{k}_2\mathbf{k}'_2\sigma'}} U_{\mathbf{k}'_1\mathbf{k}'_2;\mathbf{k}_2\mathbf{k}_1} c^\dagger_{\mathbf{k}'_1\sigma} c^\dagger_{\mathbf{k}'_2\sigma'} c_{\mathbf{k}_2\sigma'} c_{\mathbf{k}_1\sigma} \ , \tag{17}$$

where the matrix elements of the e-e interaction are given by

$$U_{\mathbf{k}'_1\mathbf{k}'_2;\mathbf{k}_2\mathbf{k}_1} = \int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, \psi^*_{\mathbf{k}'_1}(\mathbf{r}) \psi^*_{\mathbf{k}'_2}(\mathbf{r}') U(\mathbf{r}-\mathbf{r}') \psi_{\mathbf{k}_2}(\mathbf{r}') \psi_{\mathbf{k}_1}(\mathbf{r}) \ . \tag{18}$$

With our choice of basis, the single-particle part of the Hamiltonian has a diagonal representation, involving the energies of Bloch states. Denoting by $\mathcal{H}^{(1)}$ the one-electron

Hamiltonian, i.e., kinetic energy plus lattice periodic potential (called $\mathcal{H}_l^0$ in the beginning of Text 9), we have

$$\varepsilon_{\mathbf{k}} = \langle \mathbf{k}\sigma | \mathcal{H}^{(1)} | \mathbf{k}\sigma \rangle \ , \tag{19}$$

which is spin-independent and can be evaluated in the coordinate representation as

$$\varepsilon_{\mathbf{k}} = \int \mathrm{d}^3 r \ \psi_{\mathbf{k}}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) \, . \tag{20}$$

As remarked before, we are using, for simplicity, a notation without band indices, which is applicable when the relevant physical processes occur in a single band. This can be easily generalized to take into account other bands, with the biggest complication arising in the e-e interaction term, which may involve interactions between electrons in different bands.

Fermion operators in real space

It is sometimes convenient to define annihilation and creation operators in real space (i.e., coordinate space). The usual notation for fermions (e.g., in Quantum Field Theory) is $\hat{\psi}_\sigma(\mathbf{r})$ and $\hat{\psi}_\sigma^\dagger(\mathbf{r})$, respectively. Since spatial coordinates are continuous variables, these operators are interpreted as representing a *fermionic field*, and are called *field operators*. Our notation includes a *hat* to avoid confusion with wavefunctions.

In analogy to what we did in **k**-space, we can define the field operators by their action on the vacuum, i.e,

$$\hat{\psi}_\sigma^\dagger(\mathbf{r})|0\rangle \mathrel{\hat{=}} |\mathbf{r}\sigma\rangle \ , \quad \langle 0|\hat{\psi}_\sigma(\mathbf{r}) \mathrel{\hat{=}} \langle \mathbf{r}\sigma| \, , \tag{21}$$

where the "hat" over the equality sign indicates a **correspondence** between a Fock-space vector (left) and a Hilbert-space vector (right). The one-particle state $|\mathbf{r}\sigma\rangle$ is a direct product $|\mathbf{r}\rangle|\sigma\rangle$, where $|\mathbf{r}\rangle$ is a single-particle position eigenvector. So, the above operators can be viewed as creation and annihilation operators of fermions at well defined **points in space**. It is straightforward to relate them to the previously defined **k**-space operators. For instance,

$$\hat{\psi}_\sigma^\dagger(\mathbf{r})|0\rangle \mathrel{\hat{=}} |\mathbf{r}\sigma\rangle = \sum_{\mathbf{k}\sigma'} |\mathbf{k}\sigma'\rangle\langle\mathbf{k}\sigma'|\mathbf{r}\sigma\rangle = \sum_{\mathbf{k}} \psi_{\mathbf{k}\sigma}^*(\mathbf{r})|\mathbf{k}\sigma\rangle \mathrel{\hat{=}} \sum_{\mathbf{k}} \psi_{\mathbf{k}\sigma}^*(\mathbf{r}) c_{\mathbf{k}\sigma}^\dagger |0\rangle, \tag{22}$$

where $\psi_{\mathbf{k}\sigma}(\mathbf{r})$ is a Bloch-electron wavefunction. The above equation means that

$$\hat{\psi}_\sigma^\dagger(\mathbf{r}) = \sum_{\mathbf{k}} \psi_{\mathbf{k}}^*(\mathbf{r}) c_{\mathbf{k}\sigma}^\dagger \ . \tag{23}$$

Hermitian conjugation then yields

$$\hat{\psi}_\sigma(\mathbf{r}) = \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) c_{\mathbf{k}\sigma} \ , \tag{24}$$

and the inverse forms are

$$c^\dagger_{\mathbf{k}\sigma} = \int \mathrm{d}^3r\, \psi_{\mathbf{k}}(\mathbf{r})\, \hat{\psi}^\dagger_\sigma(\mathbf{r}) \,. \tag{25}$$

$$c_{\mathbf{k}\sigma} = \int \mathrm{d}^3r\, \psi^*_{\mathbf{k}}(\mathbf{r})\, \hat{\psi}_\sigma(\mathbf{r}) \,, \tag{26}$$

Consistency of the equations pairs (23)–(25) and (24)–(26) implies that

$$\sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r})\psi^*_{\mathbf{k}}(\mathbf{r}') = \sum_{\mathbf{k}} \langle \mathbf{r}|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{r}'\rangle = \langle\mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r}-\mathbf{r}') \,, \tag{27}$$

which is the expected "normalization" for eigenvectors of an operator with a continuous spectrum. From the previous relationships, one easily obtain the anticommutator for the field operators as

$$\left\{\hat{\psi}_\sigma(\mathbf{r}), \hat{\psi}^\dagger_{\sigma'}(\mathbf{r}')\right\} = \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma\sigma'}. \tag{28}$$

Finally, the occupation-number operator is replaced by a spatial-density operator

$$\hat{\rho}_\sigma(\mathbf{r}) = \hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r}) \,. \tag{29}$$

Here we see a possible justification for the expression "second quantization": by comparison with the position probability density in Quantum Mechanics, the *wave function* appears "promoted" to an *operator*. Equation (29), after summing over the spin index, provides a **density operator**, whose existence was implied in the formal construction of density functionals in our discussion of DFT (Text 9).

Wannier representation in Fock space

The electronic Hamiltonian written as in Eq. (17) corresponds to a Bloch representation in Fock space. In Text 4 we discussed the Wannier representation, which uses basis states associated to lattice sites instead of wavevectors. The Hamiltonian written in that Text can be extended to include the e-e interaction. Again we write it for the case of a single band (although it can be easily generalized to include a band index):

$$\mathcal{H} = \sum_{ij\sigma} |i\sigma\rangle\langle i\sigma|\mathcal{H}^{(1)}|j\sigma\rangle\langle j\sigma| + \frac{1}{2}\sum_{ii'\sigma}\sum_{jj'\sigma'} |i'\sigma\rangle|j'\sigma'\rangle\langle i'\sigma|\langle j'\sigma'|U|j\sigma'\rangle|i\sigma\rangle\langle j\sigma'|\langle i\sigma| \,. \tag{30}$$

In analogy to what was done in Bloch representation, to obtain the Fock-space Hamiltonian we replace the projectors by products of creation and annihilation operators. The result is

$$\mathcal{H} = \varepsilon_0 \sum_{i\sigma} c^\dagger_{i\sigma}c_{i\sigma} - \sum_{ij\sigma} t_{ij}c^\dagger_{i\sigma}c_{j\sigma} + \frac{1}{2}\sum_{ii'\sigma}\sum_{jj'\sigma'} U_{i'j',ji}c^\dagger_{i'\sigma}c^\dagger_{j'\sigma'}c_{j\sigma'}c_{i\sigma} \,, \tag{31}$$

where $c_{i\sigma}^{\dagger}$ creates an electron of spin σ in the Wannier state associated to lattice site i. It is implicitly assumed that $t_{ii} = 0$. In addition, we use the notation

$$\varepsilon_0 \equiv \langle i\sigma|\mathcal{H}^{(1)}|i\sigma\rangle \,, \tag{32}$$

$$t_{ij} \equiv -\langle i\sigma|\mathcal{H}^{(1)}|j\sigma\rangle \,, \tag{33}$$

$$U_{i'j',ji} \equiv \langle i'\sigma|\langle j'\sigma'|U|j\sigma'\rangle|i\sigma\rangle \,, \tag{34}$$

observing that the local energy ε_0, the hopping integral t_{ij}, and the matrix elements of the e-e interaction do not depend on spin.

The Coulomb-interaction matrix elements (34) generate single-site and inter-site terms (also inter-orbital, if extended to more orbitals per site). The number of interaction parameters is usually reduced in specific models, based on physical arguments of relative importance. The simplest form for a single orbital per site keeps only the fully local interaction ($i = i' = j = j'$). It is known as *Hubbard model*, and the Hamiltonian can be written as

$$\mathcal{H} = \varepsilon_0 \sum_{i\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} - \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \,, \tag{35}$$

where $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is the number operator associated to the spin-state σ at site i. This model is widely employed in the study of *strongly correlated electron systems*. For $U = 0$, Eq. (35) yields a second-quantization version of the tight-binding Hamiltonian introduced in Eq. (14) of Text 4.

It is worth remarking that the field operators $\hat{\psi}_{\sigma}(\mathbf{r})$ and $\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})$ can also be written in the Wannier representation. One just has to replace wavevectors by lattice sites, and Bloch by Wannier functions in Eqs. (23–27).

The second-quantization Hamiltonians introduced here will be starting points for our discussion of electron interactions in the remaining of this course.