SECOND QUANTIZATION

Consequences of indistinguishability

In quantum mechanics, identical particles are indistinguishable. In fact, even if we imagine that originally all particles are numbered, if we observe a particle at some place after a finite period of time, we cannot say with certainty which number it carries. This is because in quantum mechanics the notion of particle trajectory loses its sense.

Because of this fundamentally new property, the wavefunction of a two-particle system, $\psi(1,2)$ (where 1 and 2 are the coordinates -including spin- of particles 1 and 2) should be physically equivalent to $\psi(2,1)$. This means the two wavefunctions may differ only by a phase factor:

$$\psi(1,2) = e^{i\phi}\psi(2,1) = e^{2i\phi}\psi(1,2), \tag{1}$$

where in the second equation we have used the same argument once more. This means in turn that $e^{2i\phi} = 1$, which can be realized in two ways: either $e^{i\phi} = 1$ or $e^{i\phi} = -1$. It is an experimental fact that the first possibility is realized for particles with integer spin (bosons), while the second possibility is realized for particles with half-integer spin (fermions).

In condensed-matter physics, we consider electrons, protons, and neutrons as elementary particles. All of them have spin 1/2, i.e. they are fermions. So why do we speak about bosons? At not too high energies, bound states of electrons, protons, and nucleons can be considered as elementary. For instance, when dealing with liquid ^{4}He at cryogenic temperatures, we can safely neglect all the excited states of this atom. Now, since it consists of an even number of fermions (2e+2p+2n), an exchange of two helium atoms does not lead to a minus sign in the many body wavefunction, i.e. the atom ^{4}He is a boson. On the other hand, it is worth pointing out that the other stable isotope, ^{3}He, is a fermion, being composed of only five elementary particles (2e+2p+1n).

Let us start by considering the case when, in the system of interest, there is only one particle. (For definiteness, we can think of a particle in a box $L \times L \times L$ with periodic boundary conditions, $\varphi(x+L, y, z) = \varphi(x, y, z)$ and similarly in the y and z directions.) All possible states of this particle form a Hilbert space. Let $\{|a\rangle, |b\rangle, \ldots\}$ be an orthonormal basis of this Hilbert space. In the x-representation, the corresponding wavefunctions are $\varphi_a(\mathbf{x}), \varphi_b(\mathbf{x}), \ldots$

For a system with only one particle it is irrelevant, whether the particle is a boson or a fermion. Now consider that we have many identical particles in the system. We have seen that the cases of fermions and bosons should be treated separately.

Bosons

Consider first a system with two bosons in two different states $|a\rangle$ and $|b\rangle$. Then it is easy to see that the normalised two-boson wavefunction (which must be symmetric under exchange of the coordinates 1 and 2 of the first and second particle) reads

$$\psi_{1,1,0,\ldots}(1,2) = \frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\right],$$

where the index $1, 1, 0, \ldots$ denotes that states $|a\rangle$ and $|b\rangle$ are populated with one particle each, whereas all other one-particle states are empty. Now consider a general sytem of

N bosons with N_1 particles in the state $|a\rangle$, N_2 particles in the state $|b\rangle$, etc. Then the N-boson wavefunction which is symmetric under exchange of any two particles reads

$$\psi_{N_1,N_2,\ldots}(1,2,\ldots,N) = \sqrt{\frac{N_1!N_2!\ldots}{N!}} \sum_{\{P\}} \varphi_{P_1}(1)\varphi_{P_2}(2)\ldots\varphi_{P_N}(N), \tag{2}$$

where $P_1, P_2, \ldots, P_N$ is a permutation of N_1 indices a, N_2 indices b, etc. The sum is to be taken over all different permutations. It is obvious that, once the basis of single-particle states is fixed, the many-body states are completely determined by specifying the numbers of particles occupying the single-particle states. Therefore instead of the wavefunction $\psi_{N_1,N_2,\ldots}(1,2,\ldots,N)$ in $\mathbf{x}$-representation we can talk about the state $|N_1, N_2, \ldots\rangle$. Let us show now that Eq. 2 is a normalised wavefunction:

$$\begin{aligned}\langle N_1, N_2, \ldots | N_1, N_2, \ldots\rangle &= \frac{N_1!N_2!\ldots}{N!} \sum_{\{P,P'\}} \int d1 \varphi^*_{P'_1}(1)\varphi_{P_1}(1)\ldots \int dN \varphi^*_{P'_N}(N)\varphi_{P_N}(N) \\ &= \frac{N_1!N_2!\ldots}{N!} \sum_{\{P,P'\}} \delta_{P_1,P'_1}\ldots\delta_{P_N,P'_N} = 1,\end{aligned}$$

since the number of permutations is $N!/N_1!N_2!\ldots$

Any N-boson state can be written as a linear superposition of states of the type Eq. 2 which are seen to form a complete orthonormal basis of the Hilbert space of N-particle states.

From Eq. 2 one can see that the formula for the many-body wavefunction in $\mathbf{x}$-representation representation is quite cumbersome, although the physical content is simple: the wavefunction contains N_1 particles in state $|a\rangle$, N_2 particles in state $|b\rangle$, etc. In what follows we introduce an equivalent and simpler language for the description of many boson states:

- Let $|0\rangle$ be the vacuum state, i.e. a state without particles.
- Let a_i and $a_i^\dagger$ be creation and annihilation operators for the single-particle state i which satisfy the following (canonical) boson commutation relations:

$$\begin{aligned}&[a_i, a_j^\dagger] = \delta_{ij}, \\ &[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0.\end{aligned} \tag{3}$$

- Since the vacuum state contains no particles, we require that $a_i|0\rangle = 0$ for all single-particle states i.

Making use of the techniques introduced in Lecture 1, one finds readily that

$$|N_1, N_2, \ldots\rangle = \frac{1}{\sqrt{N_1!N_2!\ldots}} \left(a_a^\dagger\right)^{N_1} \left(a_b^\dagger\right)^{N_2} \ldots |0\rangle$$

is a normalized N-particle state describing the same physics as Eq. 2.

Fermions
Let us consider now systems of many fermions. For two particles in one-particle states $|a\rangle$ and $|b\rangle$, the wavefunction can be written

$$\psi_{a,b}(1,2) = \frac{1}{\sqrt{2}} \left[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right],$$

with notations similar as in the boson case. Note that, unlike in the boson case, if the states $|a\rangle$ and $|b\rangle$ are equal, the wavefunction vanishes. This implies the famous Pauli principle that two fermions can't occupy the same quantum state. It should be stressed at this point that the symbol 1 for the coordinates of the first particle should be understood as a shorthand for both the spatial and the spin coordinate, $1 = (\mathbf{x}_1, \sigma_1)$ (and similarly for other particles).

In other words, the Pauli principle implies that the sequence of occupation numbers $N_1, N_2, \ldots$ (where the ordering of the one-particle states is fixed once forever) may contain only the numbers 0 and 1. One verifies easily that the general N-particle wavefunction which is antisymmetric under exchange of any two coordinates reads

$$\psi_{a_1,a_2,\ldots,a_N}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \sum_{\{P\}} (-1)^P \varphi_{P_1}(1)\varphi_{P_2}(2)\ldots\varphi_{P_N}(N), \tag{4}$$

where $\psi_{a_1,a_2,\ldots,a_N}$ means that only the one-particle states $|a_1\rangle, |a_2\rangle, \ldots, |a_N\rangle$ are occupied and the remaining states are empty. $P_1, P_2, \ldots, P_N$ is a permutation of the states $|a_1\rangle, |a_2\rangle, \ldots, |a_N\rangle$, and the factor $(-1)^P$ equals 1 and -1 for those permutations, which can be arrived at after even and odd numbers of pair exchanges, respectively.

EXERCISE Show that the wavefunction Eq. 4 is normalized.

In what follows we adapt the method of second quantization to the case of fermions. We start with the following definitions:

- Let $|0\rangle$ be the vacuum state, i.e. a state without particles.
- Let c_i and $c_i^\dagger$ be creation and annihilation operators for the single-particle state i which satisfy the following (canonical) fermion anticommutation relations:

  $$\begin{aligned} \{c_i, c_j^\dagger\} &= \delta_{ij}, \\ \{c_i, c_j\} &= \{c_i^\dagger, c_j^\dagger\} = 0. \end{aligned} \tag{5}$$

  (The anticommutator is defined as $\{X, Y\} = XY + YX$.)
- Since the vacuum state contains no particles, we require that $c_i|0\rangle = 0$ for all single-particle states i.

In what follows we will show that the basis states of the N-fermion Hilbert space, Eq. 4, can be written in the following second-quantized form

$$|\psi_{a_1,a_2,\ldots,a_N}\rangle = c_{a_1}^\dagger c_{a_2}^\dagger \ldots c_{a_N}^\dagger |0\rangle.$$

In fact, N-particle states in which the fermions occupy different sets $\{a_1, a_2, \ldots, a_N\}$ and $\{b_1, b_2, \ldots, b_N\}$ of single-particle states are orthogonal to each other. To see this, let us assume that the state b is contained in the set $\{b_1, b_2, \ldots, b_N\}$ but not in $\{a_1, a_2, \ldots, a_N\}$. We find

$$\langle \psi_{b_1,b_2,\ldots,b_N} | \psi_{a_1,a_2,\ldots,a_N} \rangle = \langle 0 | c_{b_N} \ldots c_{b_2} c_{b_1} c^\dagger_{a_1} c^\dagger_{a_2} \ldots c^\dagger_{a_N} | 0 \rangle = 0,$$

since the annihilation operator c_b can be moved to the right so that it is the rightmost one of the $2N$ creation and annihilation operators (with possibly changing the sign of the overlap), but $c_b|0\rangle = 0$. On the other hand, we find

$$\begin{aligned} \langle \psi_{a_1,a_2,\ldots,a_N} | \psi_{a_1,a_2,\ldots,a_N} \rangle &= \langle 0 | c_{a_N} \ldots c_{a_2} c_{a_1} c^\dagger_{a_1} c^\dagger_{a_2} \ldots c^\dagger_{a_N} | 0 \rangle \\ &= \langle 0 | c_{a_N} \ldots c_{a_2} (1 - c^\dagger_{a_1} c_{a_1}) c^\dagger_{a_2} \ldots c^\dagger_{a_N} | 0 \rangle \\ &= \langle 0 | c_{a_N} \ldots c_{a_2} c^\dagger_{a_2} \ldots c^\dagger_{a_N} | 0 \rangle \\ &= \ldots \\ &= \langle 0 | 0 \rangle = 1, \end{aligned}$$

i.e. the state $|\psi_{a_1,a_2,\ldots,a_N}\rangle$ is normalized. We have used that $[c^\dagger_{a_1} c_{a_1}, c^\dagger_{a_j}] = 0$ for $j \neq 1$. Note that all states $a_1, a_2, \ldots, a_N$ must be different, otherwise $|\psi_{a_1,a_2,\ldots,a_N}\rangle = 0$ (since from the anticommutation relations it follows $c^\dagger_a c^\dagger_a = 0$), i.e. the Pauli principle is satisfied. Finally, let us note that if the set $\{b_1, b_2, \ldots, b_N\}$ is a permutation of $\{a_1, a_2, \ldots, a_N\}$, then

$$\langle \psi_{b_1,b_2,\ldots,b_N} | \psi_{a_1,a_2,\ldots,a_N} \rangle = \pm 1,$$

the plus (minus) sign obtaining for an even (odd) permutation. Thus, the order of operators is not irrelevant as in the case of bosons.

EXERCISE Show that $c^\dagger_a c_a |\psi_{a_1,a_2,\ldots,a_N}\rangle = n_a |\psi_{a_1,a_2,\ldots,a_N}\rangle$, where $n_a = 1$ if the state a is among the states $a_1, a_2, \ldots, a_N$ and $n_a = 0$ otherwise. Thus the operator $c^\dagger_a c_a$ measures the number of particles in the single-particle state a.

One-particle operators

Having defined the many-particle states in the language of second quantization, let us discuss now how to express the operators in terms of creation and annihilation operators. Let us start with the so-called one-particle operators F, which can be written as

$$F = \sum_{i=1}^{N} f_i,$$

where the sum runs over all particles in the system and f_i is an operator acting on the i-th particle. The kinetic energy, total momentum, z-component of the total spin, etc. are examples of such operators.

Let us consider that basis of one-particle states $|a\rangle, |b\rangle, \ldots$ which diagonalizes the one-particle operators f, $\langle a|f|b\rangle = f_a \delta_{ab}$. It is obvious that in this basis the total quantity F can be calculated by summing over all states and counting how many particles occupy them,

$$F = \sum_a f_a c^\dagger_a c_a = \sum_{ab} \langle a|f|b\rangle c^\dagger_a c_b$$

where for definiteness we have assumed the fermion case, but the boson case has the same form. The second equation, although at first sight unnecessarily complicated, will be used later.

Finally, let us change the basis set of one-particle states to $|\alpha\rangle = \sum_a U_{\alpha a}|a\rangle$ (the old basis states are denoted by latin and the new ones by greek letters). The hermitian conjugate equation reads $\langle\alpha| = \sum_a U^*_{\alpha a}\langle a|$ and therefore

$$\delta_{\alpha\beta} = \langle\alpha|\beta\rangle = \sum_{ab} U^*_{\alpha a} U_{\beta b}\langle a|b\rangle = \sum_a U^*_{\alpha a} U_{\beta a} = \sum_a U_{\beta a}\left(U^\dagger\right)_{a\alpha} = \left(UU^\dagger\right)_{\beta\alpha}.$$

Thus a transformation between orthonormal bases needs to be unitary, $UU^\dagger = 1$ or $U^\dagger = U^{-1}$. From here it follows that $U^\dagger U = 1$ or $\sum_a U^*_{a\alpha} U_{a\beta} = \delta_{\alpha\beta}$. The inverse transformation from the new basis to the old one therefore reads

$$\sum_\alpha U^*_{\alpha a}|\alpha\rangle = \sum_{\alpha b} U^*_{\alpha a} U_{\alpha b}|b\rangle = \sum_b \delta_{ab}|b\rangle = |a\rangle.$$

Since the wavefunctions can be thought of as a result of the action of creation operators on the vacuum, we have the following transformation rules

$$\begin{aligned} c^\dagger_a &= \sum_\alpha U^*_{\alpha a} c^\dagger_\alpha, \\ c_a &= \sum_\alpha U_{\alpha a} c_\alpha. \end{aligned} \tag{6}$$

Inserting Eq. 6 into the expression for F we find

$$F = \sum_{ab}\langle a|f|b\rangle c^\dagger_a c_b = \sum_{ab}\sum_{\alpha\beta} U^*_{\alpha a}\langle a|f|b\rangle U_{\beta b} c^\dagger_\alpha c_\beta = \sum_{\alpha\beta}\langle\alpha|f|\beta\rangle c^\dagger_\alpha c_\beta, \tag{7}$$

which is the general expression for one body operators, valid both for bosons and fermions.

Two body operators
In what follows we seek an expression for a general two-body operator

$$G = \frac{1}{2}\sum_{i\neq j} g_{ij},$$

where the sum is over all pairs of particles (we exclude the interaction of a particle with itself) and g_{ij} is an operator acting on particles i and j. The most commonly met example of a two-body operator is the interaction energy of a system with two-body interactions, e.g. the Coulomb energy of charged particles. We will frequently make use of the matrix element

$$\langle ab|g|cd\rangle = \int di \int dj\ \varphi^*_a(i)\varphi^*_b(j) g_{ij}\varphi_c(i)\varphi_d(j). \tag{8}$$

Note that $\langle ab|g|cd\rangle^* = \langle cd|g|ab\rangle$. Moreover, for even operators $g_{ij} = g_{ji}$, we also have $\langle ab|g|cd\rangle = \langle ba|g|dc\rangle$. These two properties imply that the matrix elements $\langle ab|g|ab\rangle$ and $\langle ab|g|ba\rangle$ are both real.

Let us consider that basis of single-particle states which diagonalizes the interaction function g, $\langle ab|g|cd\rangle = \delta_{ac}\delta_{bd}\langle ab|g|ab\rangle$. In this case also the two-body operator G remains diagonal in the basis Eq. 4 of the N-fermion Hilbert space (or, for N-boson states, in the basis Eq. 2). Therefore the operator G can be expressed as

$$G = \frac{1}{2}\sum_{ab}\langle ab|g|ab\rangle P_{ab},$$

where P_{ab} is an operator counting the number of particle pairs. If $|a\rangle \neq |b\rangle$ then $P_{ab} = n_a n_b$ (where n_a is the operator of the number of particles), whereas for $|a\rangle = |b\rangle$ we have $P_{aa} = n_a(n_a - 1)$. Combining the two cases, we can write $P_{ab} = n_a n_b - \delta_{ab} n_a$. In terms of creation and annihilation operators we thus obtain $P_{ab} = c_a^\dagger c_a c_b^\dagger c_b - \delta_{ab} c_a^\dagger c_a$ and therefore in our one-particle basis we can write

$$G = \frac{1}{2}\sum_{ab}\langle ab|g|ab\rangle(c_a^\dagger c_a c_b^\dagger c_b - \delta_{ab} c_a^\dagger c_a) = \frac{1}{2}\sum_{abcd}\langle ab|g|cd\rangle(c_a^\dagger c_c c_b^\dagger c_d - \delta_{cb} c_a^\dagger c_d).$$

Now we observe that making use of canonical commutation (anticommutation) relations we can write $c_a^\dagger c_c c_b^\dagger c_d - \delta_{cb} c_a^\dagger c_d = c_a^\dagger c_b^\dagger c_d c_c$, an expression valid both for fermions and bosons. If we perform the transformation Eq. 6 to a general basis, making use of

$$\sum_{abcd} U_{\alpha a}^* U_{\beta b}^* U_{\delta d} U_{\gamma c}\langle ab|g|cd\rangle = \langle\alpha\beta|g|\gamma\delta\rangle$$

we find the final result for a two-particle operator (valid both for fermions and bosons)

$$G = \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|g|\gamma\delta\rangle\; c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma. \tag{9}$$

The Hartree-Fock method

The ground state of a many particle system is seldom a single Slater determinant (in this section we restrict our discussion to the fermion case). Nevertheless, usually a good first approximation to the ground state can be obtained, if we look for that Slater determinant, which minimizes the ground state energy within the subspace of Slater-determinant states. The crucial step is to find the corresponding set of single-particle states, out of which the Slater determinant is built. This method is called the Hartree-Fock method after its inventors.

Let us assume that the wavefunctions $\varphi_{\alpha\sigma}(\mathbf{r})$ form the optimal single-particle basis we are looking for. Let furthermore $|\Psi\rangle$ be the Slater determinant formed making use of $\varphi_{\alpha\sigma}(\mathbf{r})$. Then the expectation value of the interaction energy in the Hartree-Fock state $|\Psi\rangle$ reads

$$\begin{aligned}\langle\Psi|H_{\mathrm{int}}|\Psi\rangle &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\sum_{\sigma\sigma'}\langle\alpha\beta|V|\gamma\delta\rangle\langle\Psi|c_{\alpha\sigma}^\dagger c_{\beta\sigma'}^\dagger c_{\delta\sigma'} c_{\gamma\sigma}|\Psi\rangle \\ &= \frac{1}{2}\sum_{\alpha\beta}\sum_{\sigma\sigma'}\left(\langle\alpha\beta|V|\alpha\beta\rangle n_{\alpha\sigma} n_{\beta\sigma'} - \langle\alpha\beta|V|\beta\alpha\rangle n_{\alpha\sigma} n_{\beta\sigma'}\delta_{\sigma\sigma'}\right),\end{aligned}$$

since the same states which were annihilated by $c_{\delta\sigma'} c_{\gamma\sigma}$ have to be restored back by $c_{\alpha\sigma}^\dagger c_{\beta\sigma'}^\dagger$. It is worth to emphasize that the operators $c_{\alpha\sigma}^\dagger$ and $c_{\alpha\sigma}$ create and annihilate the states $\varphi_{\alpha\sigma}(\mathbf{r})$. If we used another basis for the creation and annihilation operators, the result for $\langle\Psi|H_{\mathrm{int}}|\Psi\rangle$ would not be that simple. Making use of the definition of the matrix elements $\langle\alpha\beta|V|\gamma\delta\rangle$ and adding the kinetic energy $H_0 = \sum_i h_0(i)$ we can write the total energy $E[\Psi]$ of the state $|\Psi\rangle$ as

$$\begin{aligned}&E[\Psi] = \sum_{\alpha\sigma}\int d^3\mathbf{x}\varphi_{\alpha\sigma}^*(\mathbf{x})h_0\varphi_{\alpha\sigma}(\mathbf{x}) \\ &+\frac{1}{2}\sum_{\alpha\beta\sigma\sigma'}\int d^3\mathbf{x}\int d^3\mathbf{y}\varphi_{\alpha\sigma}^*(\mathbf{x})\varphi_{\beta\sigma'}^*(\mathbf{y})V(\mathbf{x}-\mathbf{y})\left[\varphi_{\beta\sigma'}(\mathbf{y})\varphi_{\alpha\sigma}(\mathbf{x}) - \delta_{\sigma\sigma'}\varphi_{\alpha\sigma}(\mathbf{y})\varphi_{\beta\sigma'}(\mathbf{x})\right],\end{aligned}$$

where the sums are to be taken over occupied states. Let us minimize now $E[\Psi]$ with the boundary condition $\int d^3\mathbf{x}\varphi^*_{\alpha\sigma}(\mathbf{x})\varphi_{\alpha\sigma}(\mathbf{x}) = 1$, the latter being described by a Lagrange multiplier $\varepsilon_{\alpha\sigma}$. We obtain

$$h_0\varphi_{\alpha\sigma}(\mathbf{x}) + \sum_{\beta\sigma'}\int d^3\mathbf{y}\varphi^*_{\beta\sigma'}(\mathbf{y})V(\mathbf{x}-\mathbf{y})\left[\varphi_{\beta\sigma'}(\mathbf{y})\varphi_{\alpha\sigma}(\mathbf{x}) - \delta_{\sigma\sigma'}\varphi_{\alpha\sigma}(\mathbf{y})\varphi_{\beta\sigma'}(\mathbf{x})\right] = \varepsilon_{\alpha\sigma}\varphi_{\alpha\sigma}(\mathbf{x}), \tag{10}$$

which is the Hartree-Fock equation for the optimal one-electron orbitals. Note that if $\beta\sigma' = \alpha\sigma$, the interaction term vanishes. This means that a particle does not interact with itself. Eq. 10 can be written in the form of an ordinary Schrödinger equation $H^\sigma_{HF}\varphi_{\alpha\sigma}(\mathbf{x}) = \varepsilon_{\alpha\sigma}\varphi_{\alpha\sigma}(\mathbf{x})$, where $\varepsilon_{\alpha\sigma}$ can be interpreted as the Hartree-Fock energy of the single-particle state $\varphi_{\alpha\sigma}(\mathbf{x})$. The effective Hamiltonian H_{HF} acts on a wavefunction $\varphi_\sigma(\mathbf{x})$ as follows:

$$H^\sigma_{HF}\varphi_\sigma(\mathbf{x}) = \left[h_0 + V_H(\mathbf{x})\right]\varphi_\sigma(\mathbf{x}) - \int d^3\mathbf{y}V_\sigma(\mathbf{x}-\mathbf{y})\varphi_\sigma(\mathbf{y}).$$

The potentials $V_H(\mathbf{x})$ and $V_\sigma(\mathbf{x}-\mathbf{y})$ are called the Hartree and the exchange potential, respectively. What makes the solution of Eq. 10 difficult is the fact that these potentials are not a priori known, but they rather depend on the functions $\varphi_{\alpha\sigma}(\mathbf{x})$ to be determined,

$$\begin{aligned} V_H(\mathbf{x}) &= \int d^3\mathbf{y}V(\mathbf{x}-\mathbf{y})\sum_{\alpha\sigma}\left|\varphi_{\alpha\sigma}(\mathbf{x})\right|^2, \\ V_\sigma(\mathbf{x}-\mathbf{y}) &= \sum_{\alpha}\varphi^*_{\alpha\sigma}(\mathbf{y})V(\mathbf{x}-\mathbf{y})\varphi_{\alpha\sigma}(\mathbf{x}), \end{aligned}$$

where the sums are to be taken over occupied states. The Hartree potential is easily seen to describe the (classical) average potential created by all the particles in the system, whereas the exchange potential (which depends on the spin orientation in general) represents a quantum mechanical correction discovered by Fock. Note that the exchange potential is a non-local object, which greatly complicates the solution of Eq. 10. Usually the Hartree-Fock equations can be solved only numerically by an iterative method: first try a set of orbitals, then calculate the potentials, then solve for the new orbitals using these potentials. The calculation can be stopped when the old and new orbitals do not differ any more.

EXERCISE Show that H^σ_{HF} is a hermitian operator.

Since H^σ_{HF} is hermitian, its eigenvectors can be chosen orthogonal to each other, thereby forming an orthonormal set of states.

Taking the integral of Eq. 10, one finds readily that the single-particle energies can be written as

$$\begin{aligned} \varepsilon_{\alpha\sigma} &= \int d^3\mathbf{x}\varphi^*_{\alpha\sigma}(\mathbf{x})h_0\varphi_{\alpha\sigma}(\mathbf{x}) \\ &+ \sum_{\beta\sigma'}\int d^3\mathbf{x}\int d^3\mathbf{y}\varphi^*_{\alpha\sigma}(\mathbf{x})\varphi^*_{\beta\sigma'}(\mathbf{y})V(\mathbf{x}-\mathbf{y})\left[\varphi_{\beta\sigma'}(\mathbf{y})\varphi_{\alpha\sigma}(\mathbf{x}) - \delta_{\sigma\sigma'}\varphi_{\alpha\sigma}(\mathbf{y})\varphi_{\beta\sigma'}(\mathbf{x})\right]. \end{aligned}$$

Note that there is no factor 1/2 in the term coming from interactions. This means that the total energy of the system is not a simple sum of the single-particle energies $\varepsilon_{\alpha\sigma}$, but rather

$$E = \sum_{\alpha\sigma}\varepsilon_{\alpha\sigma} - \frac{1}{2}\sum_{\alpha\sigma}\sum_{\beta\sigma'}\left(\langle\alpha\beta|V|\alpha\beta\rangle - \delta_{\sigma\sigma'}\langle\alpha\beta|V|\beta\alpha\rangle\right),$$

where the sums are once again taken over the occupied states.

As a simple example of the Hartree-Fock method, let us consider now the hydrogen molecule. Within the simplest model, we can restrict the Hilbert space of one-particle states to two orthogonal orbitals, one of them centered at the atom 1 and an identical one centered around the atom 2. We consider the following model of the hydrogen molecule 'in an external field',

$$H = -t\sum_{\sigma}(c^{\dagger}_{1\sigma}c_{2\sigma} + c^{\dagger}_{2\sigma}c_{1\sigma}) + U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}) + \Delta(n_2 - n_1). \tag{11}$$

The first term describes hopping of electrons between states $|1\rangle$ and $|2\rangle$ (parametrized by the hopping amplitude t) and the second term (in which $n_{a\sigma} = c^{\dagger}_{a\sigma}c_{a\sigma}$) originates in the Coulomb repulsion between the electrons. Note that the full Coulomb interaction $V(\mathbf{x}-\mathbf{y})$ would include also other matrix elements Eq. 8 besides

$$U = \int d^3\mathbf{x}\int d^3\mathbf{y}|\varphi_1(\mathbf{x})|^2|\varphi_1(\mathbf{y})|^2V(\mathbf{x}-\mathbf{y}) = \int d^3\mathbf{x}\int d^3\mathbf{y}|\varphi_2(\mathbf{x})|^2|\varphi_2(\mathbf{y})|^2V(\mathbf{x}-\mathbf{y}),$$

but all of them are neglected in the so-called Hubbard model Eq. 11, because they are much smaller. The term proportional to Δ describes the action of the electric field: the energy at site 2 is $+\Delta$, whereas at site 1 it is $-\Delta$. This term breaks the symmetry of the system with respect to parity.

In order to proceed, let us assume that $|\Psi\rangle = d^{\dagger}_{\uparrow}d^{\dagger}_{\downarrow}|0\rangle$ is the Slater determinant we are looking for. In other words, we assume that both the up-spin and the down-spin electrons occupy the same orbital $d^{\dagger}|0\rangle = \varphi_1 c^{\dagger}_1|0\rangle + \varphi_2 c^{\dagger}_2|0\rangle$, i.e. site i is occupied with probability amplitude φ_i. Obviously, φ_1 and φ_2 play the role of the wavefunction in our model.

EXERCISE Write down the Hartree-Fock equations for φ_1 and φ_2. Solve the equations in the limits $U = 0$ and $U \to \infty$. Calculate the difference δ of average occupations at sites 2 and 1. How does δ change under increasing U? Why?