

## 2.2 Second quantization

We introduced a compact notation for Slater determinants

$$|\Psi_S\rangle = |\psi_1 \dots \psi_N\rangle .$$

This notation hides the fact that  $|\psi_1 \dots \psi_N\rangle$  really stands for a full anti-symmetric state, which can complicate the calculations later on. That is, we must remember to keep all our states properly antisymmetric when acting on them, and also keep track of all the signs when carrying out inner products. Second quantization, in this context, is just a useful way to do the bookkeeping.

We will work without spin for now, it will be easy to reintroduce it later. For the purpose of second quantization, it is convenient to introduce a slightly different notation, called *occupation number* formalism. We first assume that the set of possible molecular orbitals  $\{\psi^{(j)}\}$  is discrete, and enumerate them with  $j \in \{1, \dots, M\}$ . The same procedure applies to any basis of wave functions for fermions, but it is important that we are assuming that the molecular orbitals are orthonormal. Then we write an occupation number vector  $|\mathbf{k}\rangle$  (a Slater determinant) as

$$|\mathbf{k}\rangle = |k_1 k_2 \dots k_M\rangle$$

where  $k_j = 1$  if the molecular orbital corresponding to the number  $j$  is present in the Slater determinant  $|\mathbf{k}\rangle$ , and is 0 otherwise. The number of electrons represented by the state  $|\mathbf{k}\rangle$  is the number of ones. We also introduce an especial vector  $|\text{vac}\rangle$ , the vacuum, corresponding to having no electrons

$$|\text{vac}\rangle = |0_1 0_2 \dots 0_M\rangle .$$

As a shorthand, we will also use the notation

$$|1_j 1_k \dots 1_l\rangle \equiv |0_1 \dots 0_{j-1} 1_j 0_{j+1} \dots 1_k \dots 1_l \dots\rangle .$$

As a matter of fact we can also use this second notation to represent ordering of molecular orbitals in the Slater determinant

$$|1_j 1_k\rangle = |\psi^{(j)} \psi^{(k)}\rangle = -|\psi^{(k)} \psi^{(j)}\rangle = -|1_k 1_j\rangle .$$

We can have a total of  $2^M$  different Slater determinants out of the set of  $M$  molecular orbitals  $\{\psi^{(j)}\}$ . For a fixed number of electrons  $N$  we can have  $M$  choose  $N$  possible Slater determinants. In general, we can have states that are linear combinations of occupation number vectors. The space spanned by occupation number vectors, which has dimension  $2^M$ , is called Fock space.

It is very important to keep in mind that the occupation number formalism is defined with respect to a basis of molecular orbitals  $\{\psi^{(j)}\}$ .

### 2.2.1 Creation and annihilation operators

Looking at the occupation number formalism, the idea of creation operators for fermions is very natural. This is even more the case if we remember the solution of the harmonic oscillator in first quantization. As it turns out, the operators that generalize the creation and annihilation operators for the harmonic oscillator give bosons. We will now review how the corresponding fermionic operators behave.

Let's then define creation operators  $a_j^\dagger$  with the property

$$a_j^\dagger|\text{vac}\rangle = |1_j\rangle .$$

This doesn't define the creation operators uniquely, because this is not yet a basis of Fock space. Remember that, because we are dealing with Slater determinants, we have

$$a_j^\dagger a_k^\dagger|\text{vac}\rangle = |1_j 1_k\rangle = -|1_k 1_j\rangle = -a_k^\dagger a_j^\dagger|\text{vac}\rangle .$$

In order to achieve the general version of this, we use the ordering of molecular orbitals that we have introduced (from 1 to  $M$ ) to define the creation operator as

$$a_p^\dagger|k_1 k_2 \dots 0_p \dots k_M\rangle = \Gamma^{\mathbf{k}}|k_1 k_2 \dots 1_p \dots k_M\rangle$$

where

$$\Gamma_p^{\mathbf{k}} = \prod_{q=1}^{p-1} (-1)^{k_q} .$$

We will check that this works shortly, but first, because  $a_p^\dagger$  is a creation operator, we define

$$a_p^\dagger|k_1 k_2 \dots 1_p \dots k_M\rangle = 0 .$$

This is due to Pauli Exclusion Principle (the wave function needs to be antisymmetric): we can not have two electrons in the same molecular orbital (ignoring spin).

Now assume, without loss of generality, that  $p < q$  and consider

$$\begin{aligned} a_p^\dagger a_q^\dagger|\dots k_p \dots k_q \dots\rangle &= \delta_{k_p 0} \delta_{k_q 0} \Gamma_p^{\mathbf{k}} \Gamma_q^{\mathbf{k}}|\dots 1_p \dots 1_q \dots\rangle \\ a_q^\dagger a_p^\dagger|\dots k_p \dots k_q \dots\rangle &= -\delta_{k_p 0} \delta_{k_q 0} \Gamma_p^{\mathbf{k}} \Gamma_q^{\mathbf{k}}|\dots 1_p \dots 1_q \dots\rangle . \end{aligned}$$

The difference in the second case is that if  $a_q^\dagger$  hits the vector after  $a_p^\dagger$  it sees the extra electron ( $p < q$ ) and the corresponding  $\Gamma$  gets an extra  $(-1)$ . In conclusion,

$$a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0 = \{a_p^\dagger, a_q^\dagger\} ,$$

where we have introduced the notation for the anti-commutator. This is the proper generalization of  $a_j^\dagger a_k^\dagger |\text{vac}\rangle = -a_j^\dagger a_k^\dagger |\text{vac}\rangle$

We are fundamentally done with our introduction to second quantization. That is, with this we have completed the definition of the creation operator in the basis of occupation number vectors, and we can now study its properties.

Here is the first one

$$a_p^\dagger a_p^\dagger = 0 .$$

This follows directly from the definition. Let's apply this operator to an arbitrary vector  $|\mathbf{k}\rangle$ , as in

$$a_p^\dagger a_p^\dagger |\mathbf{k}\rangle .$$

If the first creation operator does not give 0 is only because  $k_p = 0$  in  $\mathbf{k}$ . But then the first creation operator gives  $|\mathbf{k}'\rangle = a_p^\dagger |\mathbf{k}\rangle$  with  $k'_p = 1$ . Which implies  $a_p^\dagger |\mathbf{k}'\rangle = 0 = a_p^\dagger a_p^\dagger |\mathbf{k}\rangle$ . This is true for all  $|\mathbf{k}\rangle$ , so we are done. In words: we can never create two electrons (or fermions) in the same state, because of the Pauli Exclusion Principle. This is of course a big difference with the harmonic oscillator operators and with bosons in general.

We now look at the Hermitian adjoint of  $a_p^\dagger$ , which we write as  $a_p$ . We have

$$\langle 1_p | a_p^\dagger | 0_p \rangle = 1 = \langle 0_p | a_p | 1_p \rangle .$$

This implies that  $a_p | 1_p \rangle = | 0_p \rangle$ , and  $a_p$  is an annihilation operator. If we act on a general state we find

$$a_p |\mathbf{k}\rangle = \delta_{k_p, 1} \Gamma_p^{\mathbf{k}} |k_1 \dots 0_p \dots k_M\rangle .$$

Finally we can check the anti-commutation relations, which turn out to be the more concise way to carry out computations with fermionic operators. The anti-commutation relation for two annihilation operators follows from the adjoint of that of two creation operators. The other anti-commutation relation is left as an exercise. We write them all together for reference

$$\begin{aligned} \{a_p^\dagger, a_q^\dagger\} &= 0 \\ \{a_p, a_q\} &= 0 \\ \{a_p^\dagger, a_q\} &= \delta_{qp} . \end{aligned}$$

## 2.2.2 Change of basis

We have constructed creation and annihilation operators that work on a basis  $\{\psi^{(j)}\}$ . We can of course carry out the same procedure using a different basis of molecular orbitals  $\{\tilde{\psi}^{(j)}\}$ . Let's denote the new operators as  $\{\tilde{a}_j^\dagger\}$ .

These two basis of molecular orbitals will be related by a unitary transformation

$$\tilde{\psi}^{(j)} = \sum_k \psi^{(k)} U_{kj} .$$

Consider a Slater determinant in the new basis

$$\begin{aligned} |\tilde{\Psi}\rangle &= |\tilde{\psi}^{(j_1)} \dots \tilde{\psi}^{(j_N)}\rangle \\ &= \tilde{a}_{j_1} \dots \tilde{a}_{j_N} |\text{vac}\rangle . \end{aligned}$$

In terms of the old basis we get

$$\begin{aligned} |\tilde{\Psi}\rangle &= \sum_{k_1 \dots k_N} U_{k_1 j_1} \dots U_{k_N j_N} |\psi^{(k_1)} \dots \psi^{(k_N)}\rangle \\ &= \sum_{k_1 \dots k_N} U_{k_1 j_1} \dots U_{k_N j_N} a_{k_1}^\dagger \dots a_{k_N}^\dagger |\text{vac}\rangle . \end{aligned}$$

This gives the identification

$$\tilde{a}_j^\dagger = \sum_k a_k^\dagger U_{kj} .$$

That is, the creation operators transform as the molecular orbitals. We get the transformation for the annihilation operators taking adjoints

$$\tilde{a}_j = \sum_k a_k U_{kj}^* .$$

This unitary can be written as the exponentiation of a anti-Hermitian matrix  $\mathbf{u}$  as

$$\mathbf{U} = e^{-\mathbf{u}}, \quad \mathbf{u}^\dagger = -\mathbf{u} .$$

Consider now the interesting new operator

$$\hat{\mathbf{u}} = \sum_{pq} u_{pq} a_p^\dagger a_q, \quad \hat{\mathbf{u}}^\dagger = -\hat{\mathbf{u}} ,$$

and the even more interesting

$$\hat{\mathbf{U}} = \exp(-\hat{\mathbf{u}}) .$$

This last operator is a unitary, because  $\hat{\mathbf{u}}$  is anti-Hermitian. This operators act on Fock space. What we want to study is the transformation

$$\bar{a}_p^\dagger = \exp(-\hat{\mathbf{u}}) a_p^\dagger \exp(\hat{\mathbf{u}}) .$$

With the notation

$$\begin{aligned} \text{Ad}(U)X &= UXU^\dagger \\ \text{ad}(u)X &= [U, x] , \end{aligned}$$

we write the standard identity (from Lie group theory)

$$\text{Ad}(e^u) = e^{\text{ad}(u)} .$$

Using this identity we have

$$\bar{a}_p^\dagger = a_p^\dagger + [a_p^\dagger, \hat{\mathbf{u}}] + \frac{1}{2!} [[a_p^\dagger, \hat{\mathbf{u}}], \hat{\mathbf{u}}] + \dots$$

If you have not seen this identity before, you can easily check the first few terms expanding the exponential.

We want to evaluate these terms. To simplify the calculation, we introduce another identity

$$\begin{aligned} [A, BC] &= ABC - BCA = ABC + BAC - BAC - BCA \\ &= \{A, B\}C - B\{A, C\} . \end{aligned}$$

Applied to fermionic operators we obtain

$$[a_p^\dagger, a_q^\dagger a_r] = \{a_p^\dagger, a_q^\dagger\} a_r - a_q^\dagger \{a_p^\dagger, a_r\} = -\delta_{pr} a_q^\dagger .$$

Now is easy to evaluate the commutators with  $\hat{\mathbf{u}}$ . We get

$$\begin{aligned} [a_p^\dagger, \hat{\mathbf{u}}] &= \sum_{qr} u_{qr} [a_p^\dagger, a_q^\dagger a_r] = - \sum_{qr} u_{qr} \delta_{rp} a_q^\dagger = - \sum_q a_q^\dagger u_{qp} \\ [[a_p^\dagger, \hat{\mathbf{u}}], \hat{\mathbf{u}}] &= - \sum_q [a_q^\dagger, \hat{\mathbf{u}}] u_{qp} = \sum_{qr} a_r^\dagger u_{rq} u_{qp} = - \sum_r a_r^\dagger (\mathbf{u}^2)_{rp} . \end{aligned}$$

After a few more of these we convince ourselves that

$$\bar{a}_p^\dagger = \exp(-\hat{\mathbf{u}}) a_p^\dagger \exp(\hat{\mathbf{u}}) = \sum_k a_k^\dagger U_{kp} = \tilde{a}_p^\dagger .$$

This means that all possible Slater determinants, in any basis, are of the form

$$|\tilde{\mathbf{k}}\rangle = \prod_p (\tilde{a}_p^\dagger)^{k_p} |\text{vac}\rangle = e^{-\hat{\mathbf{u}}} \prod_p (a_p^\dagger)^{k_p} e^{\hat{\mathbf{u}}} |\text{vac}\rangle = e^{-\hat{\mathbf{u}}} \prod_p (a_p^\dagger)^{k_p} |\text{vac}\rangle = e^{-\hat{\mathbf{u}}} |\mathbf{k}\rangle .$$

The last equality follows from

$$\hat{\mathbf{u}} |\text{vac}\rangle = 0 .$$

In addition, we can take molecular orbitals to be real functions. This is because the electronic Hamiltonian being considered is real (has time reversal symmetry), so for every eigenstate, the conjugate is also an eigenstate. Which implies we can combine them to work only with real eigenstates. That means that we can also constrain the change of basis rotation to have only real parameters. Because we are working with anti-Hermitian operators, the transformation is

$$\hat{\mathbf{u}} = \sum_{p>q} u_{pq} (a_p^\dagger a_q - a_q^\dagger a_p) ,$$

where  $u_{pq}$  is now real.

### 2.2.3 One and two electron operators

We can now construct general one and two electron operators out of the fermionic creation and annihilation operators. Here is a simple one

$$n_p = a_p^\dagger a_p .$$

It is easy to check that this works as an *occupation number* operator

$$n_p | \mathbf{k} \rangle = k_p | \mathbf{k} \rangle .$$

Consider now a general one electron operator in first quantization

$$f^c = \sum_j f^c(\mathbf{x}_j) .$$

There exists some basis,  $\{\tilde{\psi}^{(j)}\}$  which diagonalizes this operator for a single electron

$$f^c = \langle \tilde{\psi}^{(j)} | f^c | \tilde{\psi}^{(j)} \rangle | \tilde{\psi}^{(j)} \rangle \langle \tilde{\psi}^{(j)} | = \tilde{f}_j | \tilde{\psi}^{(j)} \rangle \langle \tilde{\psi}^{(j)} | .$$

It is clear that in this basis the operator in second quantization must be <sup>1</sup>

$$f = \sum_j \tilde{f}_j \tilde{n}_j .$$

Using what we have just learned about changing basis we get

$$f = \sum_{pq} \left( \sum_j \tilde{f}_j U_{pj} U_{jq}^\dagger \right) a_p^\dagger a_q = \sum_{pq} f_{pq} a_p^\dagger a_q ,$$

with

$$f_{pq} = \langle \psi^{(p)} | f | \psi^{(q)} \rangle .$$

The two body operator turns out to be a little more work to get all the anti-symmetrization right. It has the form

$$g = \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q ,$$

with

$$g_{pqrs} = \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_p^*(\mathbf{x}_1) \psi_r^*(\mathbf{x}_2) g^c(\mathbf{x}_1, \mathbf{x}_2) \psi_q(\mathbf{x}_1) \psi_s(\mathbf{x}_2) .$$

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<sup>1</sup>This definition depends on the ordering chosen for the underlying molecular orbitals. This is just a freedom we have when going from the single to many fermions case.

Finally, we can write out the electronic structure Hamiltonian in second quantization. It is

$$H = h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q ,$$

with

$$h_{pq} = \int d\mathbf{r}_1 \psi_p^*(\mathbf{r}_1) \left( -\frac{1}{2} \nabla^2 - \sum_J \frac{Z_J}{r_J} \right) \psi_q(\mathbf{r}_1)$$

$$g_{pqrs} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_p^*(\mathbf{r}_1) \psi_r^*(\mathbf{r}_2) \psi_q(\mathbf{r}_1) \psi_s(\mathbf{r}_2)}{r_{12}} .$$