2.2 Second quantization

We introduced a compact notation for Slater determinants

\[ |\Psi_S\rangle = |\psi_1 \ldots \psi_N\rangle . \]

This notation hides the fact that \(|\psi_1 \ldots \psi_N\rangle\) 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 \(j \in \{1, \ldots, M\}\). 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 \(|k\rangle\) (a Slater determinant) as

\[ |k\rangle = |k_1 k_2 \ldots k_M\rangle \]

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

\[ |\text{vac}\rangle = |0102\ldots0_M\rangle . \]

As a shorthand, we will also use the notation

\[ |l_j l_k \ldots l_l\rangle \equiv |01 \ldots 0_{j-1} l_j 0_{j+1} \ldots l_k \ldots 0_{l-1} l_l\rangle . \]

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

\[ |l_j l_k\rangle = |\psi^{(j)}\psi^{(k)}\rangle = -|\psi^{(k)}\psi^{(j)}\rangle = -|l_k l_j\rangle . \]

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

$$a_j^\dagger a_k^\dagger |\text{vac}\rangle = -|1_k1_j\rangle = -a_k^\dagger a_j^\dagger |\text{vac}\rangle .$$

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

$$a_p^\dagger |k_1 k_2 \ldots 0_p \ldots k_M\rangle = \Gamma^k |k_1 k_2 \ldots 1_p \ldots k_M\rangle$$

where

$$\Gamma^k_p = \prod_{q=1}^{p-1} (-1)^{k_q} .$$

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

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

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

$$a_p^\dagger a_q^\dagger |k_p \ldots k_q \ldots\rangle = \delta_{k_p, 0} \delta_{k_q, 0} \Gamma^k_p \Gamma^k_q |1_p \ldots 1_q \ldots\rangle$$

$$a_q^\dagger a_p^\dagger |k_p \ldots k_q \ldots\rangle = -\delta_{k_p, 0} \delta_{k_q, 0} \Gamma^k_p \Gamma^k_q |1_p \ldots 1_q \ldots\rangle .$$

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,

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

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where we have introduced the notation for the anti-commutator. This is the proper generalization of $a^\dagger_j a^\dagger_k |\text{vac}\rangle = -a^\dagger_k a^\dagger_p |\text{vac}\rangle$

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

$$a^\dagger_p a^\dagger_p = 0.$$ 

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

$$a^\dagger_p a^\dagger_p |k\rangle.$$ 

If the first creation operator does not give 0 is only because $k_p = 0$ in $k$. But then the first creation operator gives $|k'\rangle = a^\dagger_p |k\rangle$ with $k'_p = 1$. Which implies $a^\dagger_p |k'\rangle = 0 = a^\dagger_p a^\dagger_p |k\rangle$. This is true for all $|k\rangle$, 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 $a^\dagger_j$, which we write as $a_j$. We have

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

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

$$a_p |k\rangle = \delta_{k_p, 1} \Gamma^p_k |1_p \ldots 0_p \ldots k_M\rangle.$$ 

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

$$\{a^\dagger_p, a^\dagger_q\} = 0$$

$$\{a_p, a_q\} = 0$$

$$\{a^\dagger_p, a_q\} = \delta_{qp}.$$ 

### 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 $\{\tilde{a}^\dagger_j\}$.

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

\[ |\tilde{\Psi}\rangle = |\tilde{\psi}^{(j_1)} \cdots \tilde{\psi}^{(j_N)}\rangle = \tilde{a}_{j_1} \cdots \tilde{a}_{j_N} |\text{vac}\rangle. \]

In terms of the old basis we get

\[ |\tilde{\Psi}\rangle = \sum_{k_1 \cdots k_N} U_{k_1j_1} \cdots U_{k_Nj_N} |\psi^{(k_1)} \cdots \psi^{(k_N)}\rangle = \sum_{k_1 \cdots k_N} U_{k_1j_1} \cdots U_{k_Nj_N} a_{k_1}^\dagger \cdots a_{k_N}^\dagger |\text{vac}\rangle. \]

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

\[ \tilde{a}_j = \sum_k a_k U_{k}^*. \]

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

\[ \tilde{a}_p^\dagger = \exp(-\hat{\mathbf{u}}) a_p^\dagger \exp(\hat{\mathbf{u}}). \]

With the notation

\[ \text{Ad}(U)X = UXU^\dagger \]
\[ \text{ad}(u)X = [U, x], \]

we write the standard identity (from Lie group theory)

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

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Using this identity we have

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

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

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

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 $\hat{u}$. We get

$$[a_p^\dagger, \hat{u}] = \sum_{qr} u_{qr}[a_p^\dagger, a_q^\dagger a_r] = -\sum_{qr} u_{qr}\delta_{rp}a_q^\dagger = -\sum_q a_q^\dagger u_{qp}$$

$$[[a_p^\dagger, \hat{u}], \hat{u}] = -\sum_q [a_q^\dagger, \hat{u}] u_{qp} = \sum_q a_q^\dagger u_{qr} u_{qp} = -\sum_q a_q^\dagger (u^2)_{rp} .$$

After a few more of these we convince ourselves that

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

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

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

The last equality follows from

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

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

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

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

\[ n_p |k\rangle = k_p |k\rangle . \]

Consider now a general one electron operator in first quantization

\[ f^c = \sum_j f^c(x_j) . \]

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

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

It is clear that in this basis the operator in second quantization must be

\[ f = \sum_j \hat{f}_j \tilde{n}_j . \]

Using what we have just learned about changing basis we get

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

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

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

\footnote{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

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

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