

# A different perspective on the Hartree Fock method

Lectures on Condensed Matter Physics

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The Hartree-Fock state of  $N$  particles can be viewed as a vacuum upon which we create excitations of particles and holes. We derive the form of the exact Hamiltonian for those excitations, and show that it takes a convenient form when expressed in the Hartree-Fock basis.

## 1 More than a variational method

Hartree-Fock (HF) theory is often presented as a variational approach to the ground state of an interacting electron system. It is that and a bit more. It also provides us with single particle basis with some interesting properties, and constitutes a fermionic version of a mean-field approximation.

The central idea of all mean-field approaches to dealing with interactions of many particles, is to assume that each particle moves independently of others, in a static mean potential, that somehow simulates interactions the other particle. For fermions, of course, the minimum energy solution of any single-particle problem consists in filling the  $N$  single particle-states with smaller energies.

We recall the main results of HF theory following Anderson [1].

The HF state that best approximates the Ground state energy, is a Slater determinant, which in second quantization, for  $N$  fermions, is

$$|\Psi_0\rangle := \prod_{i=1}^N c_i^\dagger |0\rangle = c_N^\dagger, \dots, c_1^\dagger |0\rangle \quad (1)$$

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We ordered single particle basis so that the first  $N$  states are occupied. The single particle basis, to which the  $c_i, c_i^\dagger$  refer is chosen to minimize the average energy of this  $N$  particle state, and that is what makes this an example of a variational approach. For a generic Hamiltonian with a two-body interaction

$$\mathcal{H} = \sum_{ij} t_{ij} d_i^\dagger d_j + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_i^\dagger d_j^\dagger d_l d_k \quad (2)$$

the Hartree-Fock basis, for which the Slater determinant of Eq. (1) gives the minimum energy, is the diagonal basis of single-particle Hamiltonian

$$\mathcal{H}^{HF} := \sum_{i,j} H_{ij}^{HF} d_i^\dagger d_j \quad (3)$$

defined by

$$H_{ij}^{HF} := t_{ij} + \sum_{k,l} \left( V_{jl}^{ik} - V_{lj}^{ik} \right) \left\langle d_k^\dagger d_l \right\rangle_0 \quad (4)$$

with  $\left\langle d_k^\dagger d_l \right\rangle_0$  calculated in the Hartree-Fock state of Eq. (1). Therefore in the HF basis

$$H_{ij}^{HF} := t_{ij} + \sum_{k,l} \left( V_{jl}^{ik} - V_{lj}^{ik} \right) \left\langle c_k^\dagger c_l \right\rangle_0 = \epsilon_i^{HF} \delta_{ij} \quad (5)$$

Since the occupation numbers of the HF single particle states are well defined

$$\left\langle c_k^\dagger c_l \right\rangle_0 := \langle \Psi_0 | c_k^\dagger c_l | \Psi_0 \rangle = \delta_{kl} \langle n_k \rangle_0 \quad (6)$$

The  $N$  occupied single-particle states are the ones with the  $N$  smaller HF energies,  $\epsilon_i^{HF}$ .

Solving the HF equations (Eq. (5)) involve a self-consistency cycle because the HF mean-field potential

$$\begin{aligned} \langle \varphi_j | V^{HF} | \varphi_j \rangle &:= \sum_k \left( V_{jk}^{ik} - V_{kj}^{ik} \right) \langle n_k \rangle_0 \\ &= \sum_k \left( V_{jk}^{ik} - V_{kj}^{ik} \right) \langle n_k \rangle_0 \end{aligned} \quad (7)$$

depends on the  $N$  occupied orbitals, which can only be found by diagonalizing the HF Hamiltonian.

It is illuminating to rewrite the HF potential using the explicit expression of the matrix elements of the two-body interaction

$$V_{kl}^{ij} = \int d^d r_1 d^d r_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) v(\mathbf{r}_1 - \mathbf{r}_2) \varphi_l(\mathbf{r}_2) \varphi_k(\mathbf{r}_1) \quad (8)$$

The two terms in the effective potential become

$$\langle \varphi_j | V^H | \varphi_j \rangle = \sum_k V_{jk}^{ik} \langle n_k \rangle_0 = \int d^d r_1 \varphi_i^*(\mathbf{r}_1) v^H(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_1) \quad (9)$$

with

$$v^H(\mathbf{r}_1) = \sum_k v(\mathbf{r}_1 - \mathbf{r}_2) |\varphi_k(\mathbf{r}_2)|^2 \langle n_k \rangle_0 \quad (10)$$

this is the potential created by the charge density of occupied states  $\rho(\mathbf{r}) := \sum_k |\varphi_k(\mathbf{r}_2)|^2 \langle n_k \rangle_0$ ; the second term

$$\langle \varphi_j | V^F | \varphi_j \rangle := - \sum_k V_{kj}^{ik} \langle n_k \rangle_0 = \int d^d r_1 d^d r_2 \varphi_i^*(\mathbf{r}_1) v^F(\mathbf{r}_1, \mathbf{r}_2) \varphi_j(\mathbf{r}_2) \quad (11)$$

where the Fock potential  $v^F(\mathbf{r}_1, \mathbf{r}_2)$ , also known as exchange potential, is a non-local single particle potential

We can think of the two contributions to  $\langle \varphi_j | V^H | \varphi_j \rangle$  in the following way: the electron may jump  $j \rightarrow i$  directly, due to the background potential (Hartree term), or it may excite a background electron to state  $i$  and jump to its now empty state (exchange potential). We see that the appearance of the exchange potential is related to electron indistinguishability. Notice that self-interaction of electron in the Hartree potential—the term  $k = i$  in Eq. (10),  $V_{ji}^{ii} \langle n_i \rangle_0$ —, is not excluded in the sum, but effectively cancels with the corresponding exchange term,  $-V_{ij}^{ii} \langle n_i \rangle_0$ , because  $V_{kl}^{ij} = V_{lk}^{ji}$ .

The Hartree-Fock equations then take the form

$$\sum_j \left[ t_{ij} + \sum_{k,l} (V_{jl}^{ik} - V_{lj}^{ik}) \langle d_k^\dagger d_l \rangle_0 \right] = \epsilon_i^{HF} \delta_{ij} \quad (12)$$

or in the position representation

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_e(\mathbf{r}) + V_H(\mathbf{r}) \right] \varphi_i(\mathbf{r}) + \int d^d r' v^F(\mathbf{r}' - \mathbf{r}) \varphi_i(\mathbf{r}') = \epsilon^{HF} \varphi_i(\mathbf{r}') \quad (13)$$

where  $V_e(\mathbf{r})$  is any external potential (the nuclear potential for atoms or the Lattice potential for solids)

The final result we need is the mean energy of the HF state

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \sum_i \left[ t_{ii} + \frac{1}{2} \sum_{k \text{ occ}} (V_{ik}^{ik} - V_{ki}^{ik}) \right] \quad (14)$$

with the RHS calculated in the HF basis.

The derivation of these results is presented in the next section and closely follows [1]

## 2 Derivation of HF equations

Anderson's derivation of Hartree-Fock equations can be broken down to two steps:

1. Show that for a Slater determinant state

$$|\Psi_0\rangle := \prod_{i=1}^N c_i^\dagger |0\rangle = c_N^\dagger, \dots, c_1^\dagger |0\rangle \quad (15)$$

an arbitrary infinitesimal variation is a linear combination of states of the form

$$|\delta\Psi_0\rangle = c_s^\dagger c_r |\Psi_0\rangle \quad (16)$$

where  $r$  is an occupied state in  $|\Psi_0\rangle$  and  $s$  is empty.

Obtain HF equations (12) or (13) from the extremum condition

$$\langle\delta\Psi_0|\hat{H}|\Psi_0\rangle = 0 \quad (17)$$

We start with step 1. Varying the state  $|\Psi_0\rangle$  is choosing another Slater determinant with a different set of occupied single-particle states

$$|\Psi\rangle = \prod_{i=1}^N d_i^\dagger |0\rangle \quad (18)$$

For the new basis

$$d_i = \sum_k \Lambda_{ij} c_j \quad (19)$$

If this is to be an infinitesimal variation,  $\Lambda_{ik} = \delta_{ik} + \epsilon_{ik}$  and to first order in  $\epsilon$

$$|\Psi\rangle - |\Psi_0\rangle := |\delta\Psi\rangle = \sum_r \left( \prod_{i>r} c_i^\dagger \right) \epsilon_{rs}^* c_s^\dagger \left( \prod_{i<r} c_i^\dagger \right) |0\rangle \quad (20)$$

can insert the operator  $c_r c_r^\dagger$  after  $c_s^\dagger$ , since in the state  $\left( \prod_{i<r} c_i^\dagger \right) |0\rangle$   $r$  is empty and

$$\begin{aligned} c_r c_r^\dagger \left( \prod_{i<r} c_i^\dagger \right) |0\rangle &= \left( [c_r, c_r^\dagger]_+ - c_r^\dagger c_r \right) \left( \prod_{i<r} c_i^\dagger \right) |0\rangle \\ &= ((1 - \hat{n}_r) \left( \prod_{i<r} c_i^\dagger \right) |0\rangle = \left( \prod_{i<r} c_i^\dagger \right) |0\rangle \end{aligned} \quad (21)$$

So

$$|\delta\Psi\rangle = \sum_r \left( \prod_{i>r} c_i^\dagger \right) \epsilon_{rs}^* c_s^\dagger c_r c_r^\dagger \left( \prod_{i<r} c_i^\dagger \right) |0\rangle$$

This state is only non-zero if  $s$  is not occupied in  $|\Psi_0\rangle$ ; either way, we can certainly commute the operator  $c_s^\dagger c_r$  with  $\left( \prod_{i>r} c_i^\dagger \right)$  to obtain

$$|\delta\Psi\rangle = \sum_r \epsilon_{rs}^* c_s^\dagger c_r |\Psi_0\rangle \quad (22)$$

and this completes the statement 1.

For the condition that the average energy be a minimum for the best Slater determinant, a necessary condition is

$$\delta \langle\Psi_0|\hat{H}|\Psi_0\rangle = 0 \quad (23)$$

or

$$\langle \delta\Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} | \delta\Psi_0 \rangle = 2\Re \langle \delta\Psi_0 | \hat{H} | \Psi_0 \rangle \quad (24)$$

(the Hamiltonian is hermitian) for a normalized state

$$\delta\langle \Psi_0 | \Psi_0 \rangle = \langle \delta\Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \delta\Psi_0 \rangle = 0 \quad (25)$$

Sufficient conditions are

$$\langle \delta\Psi_0 | \hat{H} | \Psi_0 \rangle = 0 \quad (26)$$

$$\langle \delta\Psi_0 | \Psi_0 \rangle = 0 \quad (27)$$

This second condition is guaranteed by any state of the form

$$|\delta\Psi\rangle = c_s^\dagger c_r |\Psi_0\rangle \quad (r \text{ occupied, } s \text{ empty}),$$

which is orthogonal to  $|\psi_0\rangle$  (it does not have the same occupation numbers). So the average energy is an extremum provided

$$\langle \delta\Psi_0 | c_r^\dagger c_s \hat{H} | \Psi_0 \rangle = 0; \quad (\text{for all } r \text{ occupied, } s \text{ empty})$$

What is left to prove is that this condition leads to Hartree-Fock equations. The strategy is to use anti-commutation relations to commute  $c_r^\dagger, c_s$  with  $\hat{H}$  because they kill the state  $|\Psi_0\rangle$ .

$$c_r^\dagger c_s \sum_{ij} t_{ij} c_i^\dagger c_j |\Psi_0\rangle = c_r^\dagger \sum_j t_{sj} c_j |\Psi_0\rangle = t_{sr} \quad (28)$$

$$\begin{aligned} c_r^\dagger c_s \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k |\Psi_0\rangle &= c_r^\dagger \frac{1}{2} \sum_{jkl} V_{kl}^{sj} c_j^\dagger c_l c_k |\Psi_0\rangle - c_r^\dagger \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_s c_j^\dagger c_l c_k |\Psi_0\rangle \\ &= c_r^\dagger \frac{1}{2} \sum_{jkl} V_{kl}^{sj} c_j^\dagger c_l c_k |\Psi_0\rangle - c_r^\dagger \frac{1}{2} \sum_{ikl} V_{kl}^{is} c_i^\dagger c_l c_k |\Psi_0\rangle \\ &= -\frac{1}{2} \sum_{jk} V_{kr}^{sj} c_j^\dagger c_k |\Psi_0\rangle + \frac{1}{2} \sum_{jl} V_{lk}^{sj} c_j^\dagger c_l |\Psi_0\rangle \\ &\quad + c_r^\dagger \frac{1}{2} \sum_{ik} V_{kr}^{is} c_i^\dagger c_k |\Psi_0\rangle - \frac{1}{2} \sum_{il} V_{rl}^{is} c_i^\dagger c_l |\Psi_0\rangle \end{aligned} \quad (29)$$

By using the symmetry  $V_{kl}^{ij} = V_{kl}^{ji}$ , and suitably relabeling of the summation indices,

$$c_r^\dagger c_s \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k |\Psi_0\rangle = \sum_{jk} \left( V_{rk}^{sj} - V_{kr}^{sj} \right) c_j^\dagger c_k |\Psi_0\rangle. \quad (30)$$

Adding the two terms, Eqs.(28) and (30), we get the extremum condition

$$t_{sr} + \sum_{jk} \left( V_{rk}^{sj} - V_{kr}^{sj} \right) \langle c_j^\dagger c_k \rangle_0 = 0; \quad s \text{ empty, } r \text{ occupied.}$$

This is the same as saying that the Hamiltonian

$$H_{sr}^{HF} := t_{sr} + \sum_{k,l} \left( V_{rk}^{sj} - V_{kr}^{sj} \right) \left\langle c_j^\dagger c_k \right\rangle_0 \quad (31)$$

has zero matrix elements between occupied and empty orbitals states. That implies that it is possible to diagonalize this Hamiltonian within the sub-spaces of occupied and empty orbitals arriving at the Hartree-Fock equations (Eq.(12))

$$H_{sr}^{HF} := t_{sr} + \sum_{k,l} \left( V_{rk}^{sj} - V_{kr}^{sj} \right) \left\langle c_j^\dagger c_k \right\rangle_0 = \epsilon_s^{HF} \delta_{sr} \quad (32)$$

### 3 New Perspective

To bring out some features of the HF basis we are going to use the HF state  $|\Psi_0\rangle$  as a reference state, a sort of vacuum, upon which we define excitations. To do that, we separate empty and filled states, and define a canonical transformation for fermion operators:

$$c_i \rightarrow c_i \quad i = N + 1, \dots, (\text{empty}) \quad (33)$$

$$c_i \rightarrow d_i^\dagger \quad i = 1, \dots, N (\text{occupied}) \quad (34)$$

This transformation preserves the canonical anti-commutation relations making  $d_i, d_i^\dagger$  ( $i = 1, \dots, N$ ) and  $c_i, c_i^\dagger$  ( $i = N + 1, N + 2, \dots$ ) *bona-fide* fermion operators that generate the complete basis of Fock space. Also  $|\Psi_0\rangle$  is a vacuum of the new electron ( $c_i$ ) and hole excitations ( $d_i$ ):

$$d_i |\Psi_0\rangle = 0 \quad (35)$$

$$c_i |\Psi_0\rangle = 0. \quad (36)$$

From here on, sums over indexes of electron operators ( $c_i, c_i^\dagger$ ) run over empty states ( $i = N + 1, \dots$ ) in  $|\Psi_0\rangle$ , and of hole operators ( $d_i, d_i^\dagger$ ) over filled ones ( $i = 1, \dots, N$ ).

It is easy to rewrite the full Hamiltonian in terms of new operators by using the replacement of Eq. 34. It will, however, no longer be in normal order with respect to the hole operators (with destruction operators to the right, killing the new vacuum). In reducing to the usual normal order we will generate terms which are constants or single particle operators.

To identify interactions among the excitations we must then reduce the Hamiltonian to normal order. Since the calculation is a bit lengthy, albeit straightforward, we state the final result. Details are given in the next section

The exact Hamiltonian in the HF basis of the  $N$  particle problem has the following form:

$$\mathcal{H} = E_0 + \mathcal{H}_{ee} + \mathcal{H}_{hh} + \mathcal{H}_{eh} + \mathcal{H}_{rcb} \quad (37)$$

- $E_0$  is the HF estimate for the ground-state energy;

- $\mathcal{H}_{ee}$  is an Hamiltonian for electrons only (empty states);

$$\mathcal{H}_{ee} = \sum_i \epsilon_i^{HF} c_i^\dagger c_i + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k \quad (38)$$

- $\mathcal{H}_{hh}$  is an Hamiltonian for holes only (in filled states)

$$\mathcal{H}_{hh} = - \sum_i \epsilon_i^{HF} d_i^\dagger d_i + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_l^\dagger d_k^\dagger d_i d_j \quad (39)$$

- $\mathcal{H}_{eh}$ ,  $\mathcal{H}_{rcb}$  are interaction terms involving electrons and holes. The first conserves the number of both types of excitations and the second one involves recombination terms, terms which change the number of electrons and holes. These terms can easily be written in normal order because we have taken care of all non-zero anti-commutators. We only have to take care of signs.

Consider this definition: if  $\hat{a}, \hat{b}, \hat{c}, \dots$  are fermion operators we define a normal ordered product,  $:\hat{a}\hat{b}\hat{c}\dots:$  (the product between colons) as

$$:\hat{a}\hat{b}\hat{c}\dots := (-1)^{\pi(\mathcal{P})} \mathcal{P}(\hat{a}\hat{b}\hat{c}\dots) \quad (40)$$

where  $\mathcal{P}(\hat{a}\hat{b}\hat{c}\dots)$  is a permutation of the order on the LHS, with all destruction operators to the right, and  $(-1)^{\pi(\mathcal{P})}$  is the parity of of the permutation (1 if the number of exchanges is even and -1 if it is odd). Inside the normal order sign,  $:\dots:$ , all fermion operators may be treated as anti-commuting. With this notation, one of the interaction terms  $\mathcal{H}_{eh}$ , conserving particle and hole number, the one arising from

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger d_j d_l^\dagger c_k \quad (41)$$

is simply

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} :c_i^\dagger d_j d_l^\dagger c_k := -\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger d_l^\dagger d_j c_k$$

because of a single fermion exchange. Another example

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} :d_i c_j^\dagger d_l^\dagger c_k := \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_j^\dagger d_l^\dagger d_i c_k \quad (42)$$

which can be combined with the previous one to give

$$-\frac{1}{2} \sum_{ijkl} (V_{kl}^{ij} - V_{lk}^{ij}) c_i^\dagger d_l^\dagger d_j c_k \quad (43)$$

We can similarly determine all terms of interaction and recombination of electrons and holes. Beware that even though we have written the Hamiltonian with all terms in normal

order, it does not follow that it kills the HF state, because there is a term that contains no destruction operators, namely

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger d_l^\dagger d_k^\dagger.$$

When acting of the “vacuum”  $|\Psi_0\rangle$  this term creates *two* particle-hole excitations. But for this term, the HF state would be an exact eigenstate of energy  $E_0$ .

Nevertheless, this form of the Hamiltonian brings out some features of the HF basis.

**Koopman’s Theorem** Consider the states with  $N + 1$  or  $N - 1$  electrons (one electron excitation of one hole excitation). If we neglect recombination terms, since we have only excitation, there are no interactions, and the Hamiltonian reduces to

$$E_0 + \sum_i \epsilon_i^{HF} c_i^\dagger c_i \quad (\text{electron excitation})$$

or

$$E_0 + \sum_i \epsilon_i^{HF} d_i^\dagger d_i \quad (\text{hole excitation}) \quad (44)$$

So the Hartree-Fock energies are excitation energies of electrons and holes, in the approximation of neglecting recombination terms. The interaction of the excitation with the  $N$  electrons of the HF ground state is included in the HF energy. This results is known as Koopman’s theorem.

**Filled Bands** Suppose that we are able to solve the  $N$  particle HF state of a completely filled band, the Hartree-Fock spectrum  $\epsilon_i^{HF}$  has a gap between the last filled state and the first empty one, but we have a total number of electrons  $N + M$ . Then we may assume the occupation of the  $N$  states are fixed (frozen) at least at low energies. This assumption is tantamount to assuming that there are no holes created in the  $N$  particle system. The effective Hamiltonian reduces in that approximation to

$$\mathcal{H} = E_0 + \mathcal{H}_{ee} = E_0 + \sum_i \epsilon_i^{HF} c_i^\dagger c_i + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k \quad (45)$$

The interactions with frozen background of  $N$  filled states, appear only as a contribution to the single particle energy of the extra electrons in the form of the Hartree-Fock potential that appears in the definition of the HF energies. An entirely similar argument can be made for a system with  $N - M$  electrons (with  $M$  holes). We now proceed to prove these result of Eq. 18.

This result separates neatly the interaction with the frozen background of  $N$  electrons from the interactions among the excitations above that state. The frozen background just provides an Hartree-Fock effective potential that appears only as a modification of the excitation single particle energies  $\epsilon_i^{HF}$ . Often, that is how we can interpret band energies, as excitation energies that include interactions with states that are “frozen” by large gaps.



### 3.1 Normal ordering

Let us first state some results. We note

$$d_i d_j^\dagger = \{d_i, d_j^\dagger\} - d_j^\dagger d_i = \delta_{ij} - d_j^\dagger d_i \quad (46)$$

If we denote the normal order

$$\begin{aligned} : d_i d_j^\dagger : &= -d_j^\dagger d_i \\ : d_j^\dagger d_i : &= d_j^\dagger d_i \end{aligned}$$

and the contraction

$$\overline{d_i d_j^\dagger} := \{d_i, d_j^\dagger\} = \delta_{ij}$$

we have

$$d_i d_j^\dagger = : d_i d_j^\dagger : + \overline{d_i d_j^\dagger}$$

Now consider more operators and check the following result

$$\begin{aligned} d_i d_j d_k^\dagger &=: d_i d_j d_k^\dagger : \quad (\text{normal order}) \\ &+ \overline{d_i d_j} d_k^\dagger + \overline{d_i d_k^\dagger} d_j \quad (\text{terms with one contraction}) \\ &= d_k^\dagger d_i d_j + \delta_{jk} d_i - \delta_{ik} d_j \end{aligned}$$

The results is the operators in normal order plus two contractions:  $j$  with  $k$  and  $i$  with  $k$ . The second gets a minus sign because there is one fermion exchange required to bring the contracted operator together. The signs of the final result are:

- +1 for first term, for there are two fermionic exchanges;
- +1 for the second term that does not involve fermionic exchanges;
- -1 for the last one because to bring contracted operators together, we need one exchange.

In the same vein

$$\begin{aligned} d_i d_j d_l^\dagger d_k^\dagger &=: d_i d_j d_l^\dagger d_k^\dagger : + \overline{d_i d_j} d_l^\dagger d_k^\dagger + \overline{d_i d_k^\dagger} d_j d_l^\dagger + \\ &+ \overline{d_i d_l^\dagger} d_j d_k^\dagger + \overline{d_i d_l^\dagger} d_k^\dagger d_j : \\ &+ \overline{d_i d_j} d_l^\dagger d_k^\dagger + \overline{d_i d_k^\dagger} d_j d_l^\dagger \\ &= d_l^\dagger d_k^\dagger d_i d_j \\ &+ d_k^\dagger d_j \delta_{il} - \delta_{ik} d_l^\dagger d_j - \delta_{jl} d_k^\dagger d_i + \delta_{jk} d_l^\dagger d_i \\ &+ \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \end{aligned}$$

Again the structure is easy to follow:

- +1 for normal order term (four fermionic exchanges);
- 4 terms with one contraction, one contraction for each of the exchanges required; sign +1 if the number of exchanges is even and  $-1$  if it is odd
- Two fully contracted terms with the signs again determined by the number of exchanges of fermions to bring contracted ones together.

## 4 The Hamiltonian in normal order

### 4.1 The single particle term $\hat{T}$

The one electron term is easy to treat:

$$\begin{aligned}
\hat{T} &:= \sum_{ij} t_{ij} c_i^\dagger c_j \rightarrow \sum_{ij} t_{ij} c_i^\dagger c_j + \sum_{ij} t_{ij} d_i d_j^\dagger + \sum_{ij} t_{ij} c_i^\dagger d_j^\dagger + \sum_{ij} t_{ij} d_i c_j \\
&= \sum_{ij} t_{ij} c_i^\dagger c_j + \sum_i t_{ii} - \sum_{ij} t_{ij} d_j^\dagger d_i + \sum_{ij} t_{ij} c_i^\dagger d_j^\dagger + \sum_{ij} t_{ij} d_i c_j \\
&= \sum_{ij} t_{ij} c_i^\dagger c_j - \sum_{ij} t_{ij} d_j^\dagger d_i \\
&\quad + \sum_{ij} t_{ij} c_i^\dagger d_j^\dagger + \sum_{ij} t_{ij} d_i c_j \\
&\quad + \sum_i t_{ii}
\end{aligned} \tag{47}$$

Recall that indexes run from 1 to  $N$  for  $d$  operators and  $N+1$  and above for  $c$  operators. The first terms are the one-particle terms for electrons and holes. The remaining terms will be combined with similar terms coming from interactions and simplified by the HF equations.

### 4.2 Interactions

To reduce interactions to normal order is more laborious; we split the calculation according to the number of hole operators in each terms.

**One of zero hole operators** Terms with zero or one operator one involve signs to reduce to normal order.

$$\begin{aligned}
\mathcal{H}_{01} &:= \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k \\
&\quad - \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger d_k^\dagger c_l + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger d_l^\dagger c_l \\
&\quad + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger d_j c_l c_k - \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_j^\dagger d_i c_l c_k
\end{aligned} \tag{48}$$

The first term is the interaction among electrons in empty states and its matrix elements are unchanged. All the other interaction terms fail to conserve the number of electrons and holes and we will call them recombination terms (the first term for instance creates an electron hole pair).

**Two hole operators** Terms with  $d_i d_j$  or  $d_i^\dagger d_j^\dagger$  are already in normal order. This term for instance creates two electron-hole excitations.

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger d_l^\dagger d_k^\dagger \quad (49)$$

More interesting are terms like

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger d_j d_l^\dagger c_k \quad (50)$$

Using the properties  $V_{kl}^{ij} = V_{lk}^{ji}$ , the anti-commutation between  $d$ 's and  $c$ 's, and relabeling the sum indexes one easy groups all those terms as

$$\begin{aligned} \mathcal{H}_2 &= \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) c_i^\dagger d_j d_l^\dagger c_k \\ &= \sum_{ik} \left[ \sum_{j \text{ occ}} \left( V_{kj}^{ij} - V_{jk}^{ij} \right) \right] c_i^\dagger c_k \\ &\quad - \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) c_i^\dagger d_l^\dagger d_j c_k \end{aligned} \quad (51)$$

The last term is an interaction between electrons and holes. The first one, however, can be combined with a one electron term of the same structure to give

$$\begin{aligned} \sum_{ij} \left[ t_{ij} + \sum_{k \text{ occ}} \left( V_{jk}^{ik} - V_{kj}^{ik} \right) \right] c_i^\dagger c_j &= \sum_{ij} H_{ij}^{HF} c_i^\dagger c_j \\ &= \sum_i \epsilon_i^{HF} c_i^\dagger c_i \end{aligned} \quad (52)$$

**Three hole operators** We have two types of terms

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_i d_j d_l^\dagger c_k \quad (53)$$

or

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_i c_j^\dagger d_l^\dagger d_k \quad (54)$$

Using the same technique as before we gather terms by using the symmetry properties of the  $V_{kl}^{ij}$  to get

$$\mathcal{H}_3 = \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) d_i d_j d_l^\dagger c_k + \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) c_i^\dagger d_j d_l^\dagger d_k^\dagger \quad (55)$$

We now reduce this to normal order by using the same technique. The first term generates a  $dc$  term the second a  $c^\dagger d^\dagger$

$$\begin{aligned} d_i d_j d_l^\dagger c_k &= d_l^\dagger d_i d_j c_k \\ &\quad - \delta_{jl} d_i c_k + \delta_{il} d_j c_k \end{aligned} \quad (56)$$

So

$$\begin{aligned} \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) d_i d_j d_l^\dagger c_k &= \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) d_l^\dagger d_i d_j c_k \\ &\quad + \frac{1}{2} \sum_{ijk} \left( V_{kj}^{ij} - V_{jk}^{ij} \right) d_i c_k - \left( V_{ki}^{ij} - V_{ik}^{ij} \right) d_j c_k \\ &= \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) d_l^\dagger d_i d_j c_k \\ &\quad + \sum_{ij} \sum_{k \text{ occ}} \left( V_{jk}^{ik} - V_{kj}^{ik} \right) d_i c_j \end{aligned} \quad (57)$$

We recall The occurrence of a similar term in the one-particle operator, which added to this one, gives

$$\sum_{ij} \left[ t_{ij} + \sum_{k \text{ occ}} \left( V_{jk}^{ik} - V_{kj}^{ik} \right) \right] d_i c_j \quad (58)$$

By definition, in the HF basis the Hartree-Fock Hamiltonian is diagonal so this term is zero because  $i$  is an occupied orbital en  $j$  an empty one. These terms are zero. A similar treatment can be made for the other type of term and the remaining terms form  $\mathcal{H}_3$  are

$$\mathcal{H}_3 = \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) d_l^\dagger d_i d_j c_k + \frac{1}{2} \sum_{ijkl} \left( V_{kl}^{ij} - V_{lk}^{ij} \right) c_i^\dagger d_l^\dagger d_k^\dagger d_j \quad (59)$$

Again these are recombination terms: the first destroys an electron hole pair and the second creates one.

**Four hole operators** This term has the form

$$\mathcal{H}_4 = \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_i d_j d_l^\dagger d_k^\dagger \quad (60)$$

We have already treat this term wham we discussed the way to normal order operators. We will get:

- The normal ordered interaction between holes:

$$\frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_l^\dagger d_k^\dagger d_i d_j \quad (61)$$

- The one electron terms

$$\begin{aligned} & \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} \left[ -\delta_{ij} d_k^\dagger d_i + \delta_{il} d_k^\dagger d_j - \delta_{ik} d_l^\dagger d_j + \delta_{kj} d_l^\dagger d_i \right] \\ &= -\frac{1}{2} \sum_{ijk} \left( V_{kj}^{ij} - V_{jk}^{ij} + V_{kj}^{ij} - V_{jk}^{ij} \right) d_k^\dagger d_i \\ &= -\sum_{ik} \sum_{j \text{ occ}} \left( V_{kj}^{ij} - V_{jk}^{ij} \right) d_k^\dagger d_i \end{aligned} \quad (62)$$

- The constant terms

$$\frac{1}{2} \sum_{ijkl} \left( V_{ij}^{ij} - V_{ji}^{ij} \right) \quad (63)$$

If we add to the one particle term

$$-\sum_{ij} t_{ij} d_j^\dagger d_i - \sum_{ij} \sum_{k \text{ occ}} \left( V_{jk}^{ik} - V_{kj}^{ik} \right) d_j^\dagger d_i \quad (64)$$

we have

$$-\sum_{ij} H_{ij}^{HF} d_j^\dagger d_i = -\sum_i \epsilon_i^{HF} d_i^\dagger d_i \quad (65)$$

and the constant terms

$$\sum_{i \text{ occ}} t_{ii} + \frac{1}{2} \sum_{ij, \text{occ}} \left( V_{ij}^{ij} - V_{ji}^{ij} \right) = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle \quad (66)$$

## 5 Summary

Our final result tend to be quite revealing:

$$\mathcal{H} = E_0 + \mathcal{H}_{ee} + \mathcal{H}_{hh} + \mathcal{H}_{eh} + \mathcal{H}_{rcb}$$

- $E_0$  is the HF estimate for the ground-state energy;
- $\mathcal{H}_{ee}$  is an Hamiltonian for electrons only (empty states)

$$\mathcal{H}_{ee} = \sum_i \epsilon_i^{HF} c_i^\dagger c_i + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} c_i^\dagger c_j^\dagger c_l c_k$$

- $\mathcal{H}_{\text{hh}}$  is an Hamiltonian for holes only (in filled states)

$$\mathcal{H}_{\text{hh}} = - \sum_i \epsilon_i^{HF} d_i^\dagger d_i + \frac{1}{2} \sum_{ijkl} V_{kl}^{ij} d_i^\dagger d_k^\dagger d_j d_l$$

- $\mathcal{H}_{\text{eh}}, \mathcal{H}_{\text{rcb}}$  are interaction terms involving electrons and holes. The first conserves the number of both types of excitations and the second one involves recombination terms. As is clear from the derivations those terms can be obtained quite simply by replacing the original 4-fermions operators by their normal ordered products. This is the result we set out to prove.

## References

- [1] Philip Warren Anderson. *Concepts in solids: lectures on the theory of solids*. Frontiers in Physics. Benjamin, New York, NY, 1964. World Scientific published in 1997 a reprint of this book.