

# Notes on the Hartree-Fock Theory

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## Abstract

These are my own notes on Hartree-Fock theory of fermions. Please let me know if you find mistake/typos. Please don't distribute these notes, since I can not guarantee their accuracy.

## 1 Hamiltonian

These are my personal notes (please don't distribute, since I can not guarantee their accuracy) that cover Hartree-Fock approximation as well as other necessary things to make a hopefully coherent story. The non-relativistic Hamiltonian for  $N$  electrons and  $M$  nuclei is

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \\ &\quad - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \\ &\quad + \sum_{A=1}^M \left(-\frac{1}{2}\nabla_A^2\right) + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}\end{aligned}$$

where I think the notation is self-explanatory, the capital letters denote the nuclei. The Born-Oppenheimer approximation assumes that, because of the mass difference, we can ignore kinetic energy of the nuclei and that the potential energy due to nuclear-nuclear interactions is a constant, which we can ignore, because the zero of energy is defined arbitrarily. I will also denote the electron-nuclei interaction as  $v_{ext}(\mathbf{r})$ . The nuclei information (i.e. coordinates and charge...) will be a set of parameters, which we are given to us and we then try to solve the electronic problem. Our Hamiltonian is

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_{i=1}^N v_{ext}(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}\end{aligned}$$

$$\hat{H}\Psi = E\Psi$$

for the many body energy and wavefunction  $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ , where  $\mathbf{x}_i = \{\mathbf{r}_i, s_i\}$ . The usual story:

$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N =$  probability of finding the system with position coordinates between  $(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$  and  $(\mathbf{r}_1 + d\mathbf{r}_1, \mathbf{r}_2 + d\mathbf{r}_2 \dots \mathbf{r}_N + d\mathbf{r}_N)$  and spin coordinates  $(s_1, s_2, \dots, s_N)$ .

The variational principle says that any function will have an energy expectation value that is greater than the true ground state, other than the exact ground state wavefunction. Proof:(Sakurai-I, page-313)

For a trial ket  $|\tilde{0}\rangle$  for the ground state of the(any) system (the system has ground state energy  $E_0$ )

$$\overline{H} = \frac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

for the complete set of states  $\{|k\rangle\}$ , where  $H|k\rangle = E_k|k\rangle$

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle \langle k | \tilde{0} \rangle$$

$$\begin{aligned}
\overline{H} &= \frac{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2 E_k}{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2} \\
&= \frac{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2 (E_k - E_0 + E_0)}{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2} \\
&= \frac{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2 (E_k - E_0)}{\sum_{k=0}^{\infty} |\langle k|\tilde{0}\rangle|^2} + E_0 \\
&\geq E_0.
\end{aligned}$$

In general the spirit of the current approach is to find the wavefunction from which the density of the system can be calculated trivially

$$\begin{aligned}
E[\Psi] &= T[\Psi] + V_{ext}[\Psi] + V_{ee}[\Psi] \\
E_0 &= \min_{\Psi} E[\Psi].
\end{aligned}$$

The Hartree-Fock approximation is one method for finding the approximate wavefunction, from which everything else is obtained.

## 2 Hartree-Fock approach

Going back to

$$\hat{H} = \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$$

### 2.1 Hartree:

If one didn't have to worry about Coulomb interaction, the Hamiltonian would be separable to single particle wavefunctions can be found

$$h(i)\phi_k(\mathbf{r}_i) = \epsilon_k\phi_k(\mathbf{r}_i)$$

The spin the particles can be included by using the single particle wavefunction  $\psi_k(\mathbf{x}_i) = \phi_k(\mathbf{r}_i)\alpha(s_i), \phi_k(\mathbf{r}_i)\beta(s_i)$  for the spin functions  $\alpha(s_i)$  and  $\beta(s_i)$ . Then the Hartree ground state wavefunction is then given by

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\dots\psi_N(\mathbf{x}_N)$$

one could use this as a variational wavefunction and ask: **which set of single particle wavefunctions  $\psi_k(r_i)$  can minimize the energy** via the variational principle. Of course, there is no guarantee that one reaches a ("true": physical ground state of the system) minimum with this approach, nevertheless this is a possibility (assuming normalization of the state).

$$\begin{aligned} E_H &= \langle \hat{H} \rangle = \sum_{i=1}^N \int \psi_i^*(\mathbf{x}_i) \left( -\frac{1}{2} \nabla_i^2 \right) \psi_i(\mathbf{x}_i) d\mathbf{x}_i + \sum_{i=1}^N \int \psi_i^*(\mathbf{x}_i) v_{ext}(\mathbf{r}_i) \psi_i(\mathbf{x}_i) d\mathbf{x}_i \\ &\quad + \sum_{i=1}^N \sum_{j>i}^N \int \int \psi_i^*(\mathbf{x}_i) \psi_j^*(\mathbf{x}_j) \frac{1}{r_{ij}} \psi_i(\mathbf{x}_i) \psi_j(\mathbf{x}_j) d\mathbf{x}_i d\mathbf{x}_j \\ E_H &= \sum_{i=1}^N \int \psi_i^*(\mathbf{x}_i) \left( -\frac{1}{2} \nabla_i^2 \right) \psi_i(\mathbf{x}_i) d\mathbf{x}_i + \sum_{i=1}^N \int |\psi_i(\mathbf{x}_i)|^2 v_{ext}(\mathbf{r}_i) d\mathbf{x}_i \\ &\quad + \sum_{i=1}^N \sum_{j>i}^N \int \int \frac{|\psi_i(\mathbf{x}_i)|^2 |\psi_j(\mathbf{x}_j)|^2}{r_{ij}} d\mathbf{x}_i d\mathbf{x}_j. \end{aligned}$$

The above equation is what I would have written if I had to guess the energy for a classical electron gas would be, i.e. just the addition of kinetic energy, the classical Coulomb energy and the external energy of the system (of course there would be no wavefunctions in the classical picture). The above wavefunction  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\dots\psi_N(\mathbf{x}_N)$  has no correlation in it. This is easy to see since the probability of finding a particle with coordinates  $\mathbf{x}_i$  is independent of all other particles, since the function is separable. Another problem is that the wavefunction does not satisfy the Pauli exclusion principle (this is nonrelativistic quantum mechanics, so we have to enforce Pauli exclusion principle by hand).

## 2.2 Hartree-Fock

Lets consider a two particles system, one could write the following wavefunction that would satisfy the Pauli exclusion principle

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} (\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1))$$

which is obviously anti-symmetric under exchange of the two particles

$$\begin{aligned} \Psi(\mathbf{x}_2, \mathbf{x}_1) &= \frac{1}{\sqrt{2}} (\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1) - \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)) = -\Psi(\mathbf{x}_1, \mathbf{x}_2) \\ \Psi(\mathbf{x}_2, \mathbf{x}_1) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}} \det(\psi_1 \psi_2) \end{aligned}$$

note that  $\Psi(\mathbf{x}, \mathbf{x}) = 0$ , which is nice. We then generalize the above antisymmetrization to  $N$  particles and write the  $N$  particle Slater determinant:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \cdot & \cdot & \cdot & \psi_N(\mathbf{x}_1) \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \cdot & & & & \cdot \\ \psi_1(\mathbf{x}_N) & \cdot & \cdot & \cdot & \psi_N(\mathbf{x}_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \det(\psi_1 \psi_2 \dots \psi_N). \end{aligned}$$

"The Hartree-Fock approximation is the method whereby the orthonormal orbits  $\psi_i$  are found that minimize [the energy] for this determinantal form of  $\Psi$ ." Now we can evaluate the energy expectation value (Parr-Yang page-7 and long derivation in Szabo and Ostlund)

$$\begin{aligned} E_{HF} &= \int \dots \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \\ E_{HF}[\{\psi_j\}] &= \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \end{aligned}$$

where

$$\begin{aligned} H_i &= \int \psi_i^*(\mathbf{x}) \left[ -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) \right] \psi_i(\mathbf{x}) d\mathbf{x} \\ J_{ij} &= \iint \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = \iint |\psi_i(\mathbf{x}_1)|^2 \frac{1}{r_{12}} |\psi_j(\mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \\ K_{ij} &= \iint \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned}$$

it is important to note that the self interaction (SI) term is taken care of very beautifully (and I think accidentally) in the Hartree-Fock approximation.

$$\begin{aligned} J_{ii} &= \iint \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i^*(\mathbf{x}_2) \psi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ K_{ii} &= \iint \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2) \psi_i^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ J_{ii} - K_{ii} &= 0 \end{aligned}$$

This SI energy is a problem for some of the more sophisticated many body methods, that is why I find it interesting that HF, i.e. the simplest approximation seems to deal with it in such a nice way, I think this just say Pauli exclusion

principle is fully taken care of, whereas in other approximations, this might not be true, *but this is just a guess*.

Now we will use the Lagrange multiplier method to minimize the above energy with respect to the wavefunctions  $\psi_i$  using the constraint

$$\int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} = \delta_{ij}$$

i.e.

$$\delta(E_{HF}[\{\psi_j\}] - \sum_{ij} \epsilon_{ij} (\int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij})) = 0$$

which gives

$$\begin{aligned} \frac{\partial}{\partial \psi_k^*} E_{HF}[\{\psi_j\}] - \sum_{ij} \epsilon_{ij} \frac{\partial}{\partial \psi_k^*} \left( \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij} \right) &= 0 \\ \frac{\partial}{\partial \psi_k^*} \left[ \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \right] - \sum_{ij} \epsilon_{ij} \frac{\partial}{\partial \psi_k^*} \left( \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij} \right) &= 0 \\ \sum_{i=1}^N \frac{\partial}{\partial \psi_k^*} H_i + \frac{1}{2} \sum_{i,j=1}^N \left( \frac{\partial}{\partial \psi_k^*} J_{ij} - \frac{\partial}{\partial \psi_k^*} K_{ij} \right) - \sum_{ij} \epsilon_{ij} \frac{\partial}{\partial \psi_k^*} \left( \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij} \right) &= 0 \end{aligned}$$

$$\begin{aligned} & \left[ -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) \right] \psi_k(\mathbf{x}) d\mathbf{x} \\ & + \frac{1}{2} \frac{\partial}{\partial \psi_k^*} \sum_{j=1}^N \iint \psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & + \frac{1}{2} \frac{\partial}{\partial \psi_k^*} \sum_{i=1}^N \iint \psi_i^*(\mathbf{x}_1)\psi_i(\mathbf{x}_1) \frac{1}{r_{12}} \psi_k^*(\mathbf{x}_2)\psi_k(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & - \frac{1}{2} \frac{\partial}{\partial \psi_k^*} \sum_{j=1}^N \iint \psi_k^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_k(\mathbf{x}_2)\psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & - \frac{1}{2} \frac{\partial}{\partial \psi_k^*} \sum_{i=1}^N \iint \psi_i^*(\mathbf{x}_1)\psi_k(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2)\psi_k^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & = - \sum_j \epsilon_{kj} \frac{\partial}{\partial \psi_k^*} \left( \int \psi_k^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij} \right) \end{aligned}$$

$$\begin{aligned}
& [-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r})]\psi_k(\mathbf{x})d\mathbf{x} \\
& + \sum_{j=1}^N \int \psi_j^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)\frac{1}{r_{12}}d\mathbf{x}_2\psi_k(\mathbf{x}_1) \\
& - \sum_{j=1}^N \int \psi_j(\mathbf{x}_1)\frac{1}{r_{12}}\psi_j^*(\mathbf{x}_2)\psi_k(\mathbf{x}_2)d\mathbf{x}_2 \\
& = \sum_j \epsilon_{kj} \frac{\partial}{\partial \psi_k^*} \left( \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} - \delta_{ij} \right)
\end{aligned}$$

By simply carrying through the derivatives (and the complex conjugate of the above analysis), one ends up Par-Yang equation-1.3.7-1.3.12

$$\begin{aligned}
\widehat{F}\psi_i(\mathbf{x}) &= \sum_{j=1}^N \epsilon_{ij}\psi_j(\mathbf{x}) \\
\widehat{F} &= -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + \widehat{j} - \widehat{k} \\
\widehat{j}(\mathbf{x}_1)f(\mathbf{x}_1) &= \sum_{k=1}^N \int \psi_k^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)\frac{1}{r_{12}}f(\mathbf{x}_1)d\mathbf{x}_2 \\
\widehat{k}(\mathbf{x}_1)f(\mathbf{x}_1) &= \sum_{k=1}^N \int \psi_k^*(\mathbf{x}_2)f(\mathbf{x}_2)\frac{1}{r_{12}}\psi_k(\mathbf{x}_1)d\mathbf{x}_2
\end{aligned}$$

the general form  $\widehat{F}\psi_i(\mathbf{x}) = \sum_{j=1}^N \epsilon_{ij}\psi_j(\mathbf{x})$  include the general Lagrange multipliers  $\epsilon_{ij}$ , which is Hermitian, i.e.  $\epsilon_{ij} = \epsilon_{ji}^*$ . I will come back to this in a minute. From the above equation

$$\begin{aligned}
\int \psi_i^*(\mathbf{x})\widehat{F}\psi_i(\mathbf{x})d\mathbf{x} &= \sum_{i=1}^N \epsilon_{ij} \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} = \epsilon_{ii} = \epsilon_i \\
&= H_i + \sum_{j=1}^N (J_{ij} - K_{ij})
\end{aligned}$$

summing over  $i$

$$\begin{aligned}
\sum_{i=1}^N \epsilon_i &= \sum_{i=1}^N H_i + \sum_{i,j=1}^N (J_{ij} - K_{ij}) \\
\sum_{i=1}^N \epsilon_i &= \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij})
\end{aligned}$$

but we already know that

$$E_{HF} = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij})$$

therefore

$$\begin{aligned} \sum_{i=1}^N \epsilon_i &= E_{HF} + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \\ E_{HF} &= \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \end{aligned}$$

The term  $\frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij})$  is exactly the total Coulomb contribution to the Hartree-Fock Theory. An important point that we will come back to in DFT is that  $E_{HF} \neq \sum_{i=1}^N \epsilon_i$  (There is a, somewhat physical, discussion of this term on page 124 or Szabo/Ostlund). So the above discussion gives the equations

$$\hat{F}\psi_i(\mathbf{x}) = \sum_{i=1}^N \epsilon_{ij} \psi_j(\mathbf{x})$$

we can always change the basis as to diagonalize the matrix  $\epsilon$ , see pages 10-11 of Parr-Yang and page-120 of Szabo-Ostlund. Therefore one has to deal with

$$\hat{F}\psi_i(\mathbf{x}) = \epsilon_i \psi_j(\mathbf{x}).$$

From the expression for

$$\begin{aligned} J_{ij} &= \iint \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_1) \frac{1}{r_{12}} \psi_j^*(\mathbf{x}_2) \psi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ K_{ij} &= \iint \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) \frac{1}{r_{12}} \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned}$$

it is clear that the Hartree-Fock equations are self-consistent equations that have to be solved iteratively. In practice, to solve Hartree-Fock equations, one can introduce a fixed basis and span the unknown single particle wavefunctions in that basis. This leads to matrix equations and hence an eigenvalue/eigenvector problem (see page 136-rest of chapter 3 of Szabo and Ostlund).

$$\begin{aligned} \psi_i(\mathbf{x}) &= \sum_{\mu=1}^K C_{i\mu} \phi_{\mu}(\mathbf{x}) \\ i &= 1 \dots K \end{aligned}$$



where the set  $\{\phi_\mu\}$  is a set of known functions. If the set is complete, this would give exact solutions, and any complete set of basis could be used. In practice, since one can only deal with finite matrices, the choice of basis is important. Different forms of the expansions are appropriate for a given problem at hand. "In the case of the restricted closed-shell Hartree Fock one gets the "Roothaan" equations, whereas for unrestricted open-shell Hartree-Fock, one has "Pople-Nesbet" equations." For a detailed discussion, see sections 3.4-3.8 of Szabo-Ostlund.

**The exchange term:** I want to go back and look at the exchange term and consider two electrons.

$$\begin{aligned}
|\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2 d\mathbf{x}_1 d\mathbf{x}_2 &= \frac{1}{2} |\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1) - \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \\
&= \frac{1}{2} (\psi_1^*(\mathbf{x}_2)\psi_2^*(\mathbf{x}_1) - \psi_1^*(\mathbf{x}_1)\psi_2^*(\mathbf{x}_2)) (\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_1) - \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)) d\mathbf{x}_1 d\mathbf{x}_2 \\
&= \frac{1}{2} \begin{pmatrix} |\psi_1(\mathbf{x}_2)|^2 |\psi_2(\mathbf{x}_1)|^2 + |\psi_1(\mathbf{x}_1)|^2 |\psi_2(\mathbf{x}_2)|^2 \\ -\psi_1^*(\mathbf{x}_1)\psi_2(\mathbf{x}_1)\psi_2^*(\mathbf{x}_2)\psi_1(\mathbf{x}_2) \\ -\psi_1(\mathbf{x}_1)\psi_2^*(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\psi_1^*(\mathbf{x}_2) \end{pmatrix} d\mathbf{x}_1 d\mathbf{x}_2
\end{aligned}$$

the probability of finding the particle 1 at space coordinates 1 and particle 2 at space coordinate 2, is obtained by by integrating over the spin degrees of freedom:  $P(\mathbf{r}_1, \mathbf{r}_2)$

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \begin{pmatrix} \int \int |\psi_1(\mathbf{x}_2)|^2 |\psi_2(\mathbf{x}_1)|^2 ds_1 ds_2 \\ + \int \int |\psi_1(\mathbf{x}_1)|^2 |\psi_2(\mathbf{x}_2)|^2 ds_1 ds_2 \\ - \int \int \psi_1^*(\mathbf{x}_1)\psi_2(\mathbf{x}_1)\psi_2^*(\mathbf{x}_2)\psi_1(\mathbf{x}_2) ds_1 ds_2 \\ - \int \int \psi_1(\mathbf{x}_1)\psi_2^*(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\psi_1^*(\mathbf{x}_2) ds_1 ds_2 \end{pmatrix}$$

Case-1: two fermions with different spins

$$\begin{aligned}
\psi_1(\mathbf{x}_1) &= \phi_1(\mathbf{r}_1)\alpha(s_1) \\
\psi_1(\mathbf{x}_2) &= \phi_1(\mathbf{r}_2)\alpha(s_2)
\end{aligned}$$

$$\begin{aligned}
\psi_2(\mathbf{x}_1) &= \phi_2(\mathbf{r}_1)\beta(s_1) \\
\psi_2(\mathbf{x}_2) &= \phi_2(\mathbf{r}_2)\beta(s_2)
\end{aligned}$$

$$\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{2} \left( \int \int |\psi_1(\mathbf{x}_2)|^2 |\psi_2(\mathbf{x}_1)|^2 ds_1 ds_2 + \int \int |\psi_1(\mathbf{x}_1)|^2 |\psi_2(\mathbf{x}_2)|^2 ds_1 ds_2 \right. \\
&\quad \left. - \phi_1^*(\mathbf{r}_1) \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2) \int \alpha^*(s_1) \beta(s_1) ds_1 \int \beta^*(s_2) \alpha(s_2) ds_2 \right. \\
&\quad \left. - \int \int \psi_1(\mathbf{x}_1) [\psi_2(\mathbf{x}_1)]^* \psi_2(\mathbf{x}_2) [\psi_1(\mathbf{x}_2)]^* ds_1 ds_2 \right) \\
&= \frac{1}{2} \left( |\phi_1(\mathbf{x}_2)|^2 |\phi_2(\mathbf{x}_1)|^2 + |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \right)
\end{aligned}$$

Case-2: two fermions with the same spin

$$\psi_1(\mathbf{x}_1) = \phi_1(\mathbf{r}_1) \alpha(s_1)$$

$$\psi_1(\mathbf{x}_2) = \phi_1(\mathbf{r}_2) \alpha(s_2)$$

$$\psi_2(\mathbf{x}_1) = \phi_2(\mathbf{r}_1) \alpha(s_1)$$

$$\psi_2(\mathbf{x}_2) = \phi_2(\mathbf{r}_2) \alpha(s_2)$$

$$\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{2} \left( |\phi_1(\mathbf{x}_2)|^2 |\phi_2(\mathbf{x}_1)|^2 ds_1 ds_2 + |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \right. \\
&\quad \left. - \int \int [\psi_1(\mathbf{x}_1)]^* \psi_2(\mathbf{x}_1) [\psi_2(\mathbf{x}_2)]^* \psi_1(\mathbf{x}_2) ds_1 ds_2 \right. \\
&\quad \left. - \int \int \psi_1(\mathbf{x}_1) [\psi_2(\mathbf{x}_1)]^* \psi_2(\mathbf{x}_2) [\psi_1(\mathbf{x}_2)]^* ds_1 ds_2 \right) \\
&= \frac{1}{2} \left( |\phi_1(\mathbf{x}_2)|^2 |\phi_2(\mathbf{x}_1)|^2 ds_1 ds_2 + |\phi_1(\mathbf{x}_1)|^2 |\phi_2(\mathbf{x}_2)|^2 \right. \\
&\quad \left. - 2 \operatorname{Re} (\phi_1^*(\mathbf{r}_1) \phi_2(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \phi_1(\mathbf{r}_2)) \right)
\end{aligned}$$

Note the minus sign, the electron density includes a "hole" (Fermi hole) due to Pauli exclusion principle. This is simply saying that **Pauli exclusion principle keeps electrons away from each other independent of the repulsive Coulomb interaction**. We will come back to this in the context of density matrices. The correlation energy is, usually, defined as the energy beyond Hartree-Fock energy

$$E_{corr} = E - E_{HF}.$$

### 3 density matrix language

*This section follows closely chapter 2 of Parr-Yang.* I will first review the usual density matrix formalism for both pure (the extended formalism for mixed states is discussed in Parr-Yang, for example) and then go on to essentially write the expectation value of a general Hamiltonian, using density matrices, which will be then useful to see what is meant by HF and beyond....etc. For a pure state

of  $N$  interacting particles  $|\Psi\rangle$ , the density matrix ( $\gamma$  is used here, because  $\rho$  is sometimes used for density)

$$\hat{\gamma}_N = |\Psi\rangle\langle\Psi|$$

the real space representation is then

$$\begin{aligned}\langle\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \hat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle &= \langle\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \Psi\rangle\langle\Psi | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle \\ &= \Psi(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\end{aligned}$$

the usual properties of the pure state density matrix are

$$\begin{aligned}tr(|\Psi\rangle\langle\Psi|) &= \int \langle\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \hat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \int \langle\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \Psi\rangle\langle\Psi | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle d\mathbf{x}_1 \dots d\mathbf{x}_N = 1\end{aligned}$$

which is the normalization condition. Also

$$\begin{aligned}\hat{\gamma}_N \cdot \hat{\gamma}_N &= |\Psi\rangle\langle\Psi|\Psi\rangle\langle\Psi| = \hat{\gamma}_N \\ tr(\hat{\gamma}_N^2) &= 1\end{aligned}$$

one can define the following useful reduced-density matrices

$$\begin{aligned}&\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) \\ &= \frac{N(N-1)}{2} \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) d\mathbf{x}_3 \dots d\mathbf{x}_N\end{aligned}$$

and

$$\gamma_1(\mathbf{x}'_1; \mathbf{x}_1) = N \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N$$

then

$$\begin{aligned}tr(\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2)) &= \iint \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ &= \frac{N(N-1)}{2} \times \\ &\quad \int \dots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_N \\ &= \frac{N(N-1)}{2}\end{aligned}$$

$$\begin{aligned}
tr(\gamma_1(\mathbf{x}'_1; \mathbf{x}_1)) &= \int \gamma_1(\mathbf{x}_1; \mathbf{x}_1) d\mathbf{x}_1 \\
&= N \int \cdots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \\
&= N
\end{aligned}$$

also

$$\begin{aligned}
\gamma_1(\mathbf{x}'_1; \mathbf{x}_1) &= \frac{2}{N-1} \int \gamma_2(\mathbf{x}'_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2 \\
&= \frac{2}{N-1} \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{x}'_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_N \\
&= \gamma_1(\mathbf{x}'_1; \mathbf{x}_1)
\end{aligned}$$

Also  $\gamma_1(\mathbf{x}_1; \mathbf{x}_1) \geq 0$  and  $\gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) \geq 0$  (i.e. are semidefinite) and Hermitian

$$\begin{aligned}
\gamma_1(\mathbf{x}'_1; \mathbf{x}_1) &= \gamma_1^*(\mathbf{x}_1; \mathbf{x}'_1) \\
\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) &= \gamma_2^*(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)
\end{aligned}$$

and from the antisymmetry of the wavefunction with respect to exchange of particles, any reduced density matrix changes its sign on exchange of two primed or two unprimed particle indices.

$$\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) = -\gamma_2(\mathbf{x}'_2, \mathbf{x}'_1; \mathbf{x}_1, \mathbf{x}_2) = -\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_2, \mathbf{x}_1) = \gamma_2(\mathbf{x}'_2, \mathbf{x}'_1; \mathbf{x}_2, \mathbf{x}_1)$$

as usual the expectation value of any operator is then

$$\begin{aligned}
\langle \hat{A} \rangle &= tr(\hat{A} \hat{\gamma}_N) = tr(\hat{\gamma}_N \hat{A}) \\
&= \int \langle \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \hat{\gamma}_N \hat{A} | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N \rangle d\mathbf{x}'_1 \dots d\mathbf{x}'_N \\
&= \int \langle \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \hat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \hat{A} | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N \rangle d\mathbf{x}'_1 d\mathbf{x}'_2 \dots d\mathbf{x}'_N d\mathbf{x}_1 \dots d\mathbf{x}_N
\end{aligned}$$

If  $\hat{A}$  is a single particle operator of the form

$$\hat{A} = \sum_{i=1}^N \hat{A}(\mathbf{x}_i, \mathbf{x}'_i)$$

then

$$\begin{aligned}
\langle \hat{A} \rangle &= \sum_{i=1}^N \int \langle \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \hat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle \times \\
&\quad \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \hat{A}(\mathbf{x}_i, \mathbf{x}'_i) | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N \rangle d\mathbf{x}_1 d\mathbf{x}'_1 \dots d\mathbf{x}_N d\mathbf{x}'_N \\
&= \sum_{i=1}^N \int \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}'_i, \dots, \mathbf{x}_N | \hat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N \rangle \times \\
&\quad \langle \mathbf{x}_i | \hat{A}(\mathbf{x}_i, \mathbf{x}'_i) | \mathbf{x}'_i \rangle d\mathbf{x}_1 \dots d\mathbf{x}_i d\mathbf{x}'_i \dots d\mathbf{x}_N \\
&= \sum_{i=1}^N \int \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}'_i, \dots, \mathbf{x}_N | \Psi \rangle \langle \Psi | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N \rangle \times \\
&\quad \langle \mathbf{x}_i | \hat{A}(\mathbf{x}_i, \mathbf{x}'_i) | \mathbf{x}'_i \rangle d\mathbf{x}_1 \dots d\mathbf{x}_i d\mathbf{x}'_i \dots d\mathbf{x}_N \\
&= \sum_{i=1}^N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}'_i, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N) \times \\
&\quad \langle \mathbf{x}_i | \hat{A}(\mathbf{x}_i, \mathbf{x}'_i) | \mathbf{x}'_i \rangle d\mathbf{x}_1 \dots d\mathbf{x}_i d\mathbf{x}'_i \dots d\mathbf{x}_N \\
&\text{but} \\
\gamma_1(\mathbf{x}'_1; \mathbf{x}_1) &= N \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N \\
\langle \hat{A} \rangle &= \frac{1}{N} \sum_{i=1}^N \int \gamma_1(\mathbf{x}'_i; \mathbf{x}_i) \langle \mathbf{x}_i | \hat{A}(\mathbf{x}_i, \mathbf{x}'_i) | \mathbf{x}'_i \rangle d\mathbf{x}_i d\mathbf{x}'_i \\
\langle \hat{A} \rangle &= \frac{1}{N} \sum_{i=1}^N \int \gamma_1(\mathbf{x}'_i; \mathbf{x}_i) A(\mathbf{x}_i, \mathbf{x}'_i) d\mathbf{x}_i d\mathbf{x}'_i
\end{aligned}$$

I don't quite understand equation 2.3.22 of Parr-Yang where they seem to have reduced everything to particle-1!!

$$\langle \hat{A} \rangle_{Parr-Yang} = \int \gamma_1(\mathbf{x}'_1; \mathbf{x}_1) A(\mathbf{x}_1, \mathbf{x}'_1) d\mathbf{x}_1 d\mathbf{x}'_1$$

For a two particle operator then (assumed to be local)

$$\hat{B} = \sum_{i,j=1}^N \hat{B}(\mathbf{x}_i, \mathbf{x}_j)$$

$$\begin{aligned}
\langle \widehat{B} \rangle &= \sum_{i,j=1}^N \int \langle \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \widehat{\gamma}_N | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle \\
&\quad \times \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \widehat{B}(\mathbf{x}_i, \mathbf{x}_j) | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N \rangle d\mathbf{x}_1 d\mathbf{x}'_1 \dots d\mathbf{x}_N d\mathbf{x}'_N \\
&= \sum_{i,j=1}^N \int \langle \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N | \Psi \rangle \langle \Psi | \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N \rangle \times \\
&\quad \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N | \widehat{B}(\mathbf{x}_i, \mathbf{x}_j) | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N \rangle d\mathbf{x}_1 d\mathbf{x}'_1 \dots d\mathbf{x}_N d\mathbf{x}'_N \\
&= \sum_{i,j=1}^N \int \Psi(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \\
&\quad \langle \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \mathbf{x}_j, \dots, \mathbf{x}_N | \widehat{B}(\mathbf{x}_i, \mathbf{x}_j) | \mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_i, \mathbf{x}'_j, \dots, \mathbf{x}'_N \rangle d\mathbf{x}_1 d\mathbf{x}'_1 \dots d\mathbf{x}_N d\mathbf{x}'_N \\
&= \sum_{i,j=1}^N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}'_i, \mathbf{x}'_j, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \mathbf{x}_j, \dots, \mathbf{x}_N) \times \\
&\quad \langle \mathbf{x}_i, \mathbf{x}_j | \widehat{B}(\mathbf{x}_i, \mathbf{x}_j) | \mathbf{x}'_i, \mathbf{x}'_j \rangle d\mathbf{x}_1 \dots d\mathbf{x}'_i d\mathbf{x}'_j d\mathbf{x}_i d\mathbf{x}_j \dots d\mathbf{x}_N \\
&= \frac{2}{N(N-1)} \sum_{i,j=1}^N \int \gamma_2(\mathbf{x}'_i, \mathbf{x}'_j; \mathbf{x}_i, \mathbf{x}_j) \langle \mathbf{x}_i, \mathbf{x}_j | \widehat{B}(\mathbf{x}_i, \mathbf{x}_j) | \mathbf{x}'_i, \mathbf{x}'_j \rangle d\mathbf{x}'_i d\mathbf{x}'_j d\mathbf{x}_i d\mathbf{x}_j \\
\langle \widehat{B} \rangle &= \frac{2}{N(N-1)} \sum_{i,j=1}^N \int \gamma_2(\mathbf{x}_i, \mathbf{x}_j; \mathbf{x}_i, \mathbf{x}_j) B(\mathbf{x}_i, \mathbf{x}_j) d\mathbf{x}_i d\mathbf{x}_j
\end{aligned}$$

again

$$\begin{aligned}
&\frac{2}{N(N-1)} \gamma_2(\mathbf{x}'_i, \mathbf{x}'_j; \mathbf{x}_i, \mathbf{x}_j) \\
&= \int \dots \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}'_i, \mathbf{x}'_j, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \mathbf{x}_j, \dots, \mathbf{x}_N) \times \\
&\quad d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}'_{i-1} d\mathbf{x}'_{j-1} d\mathbf{x}_{i-1} d\mathbf{x}_{j-1} d\mathbf{x}'_{i+1} d\mathbf{x}'_{j+1} d\mathbf{x}_{i+1} d\mathbf{x}_{j+1} \dots d\mathbf{x}_N
\end{aligned}$$

and again, I am not getting Parr-Yang equation 2.3.26

$$\langle \widehat{B} \rangle_{Parr-Yang} = \int [\gamma_2(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) B(\mathbf{x}_1, \mathbf{x}_2)]_{x'_1=x_1, x'_2=x_2} d\mathbf{x}_1 d\mathbf{x}_2$$

nevertheless it is clear that total energy can be written as (at least of the form)

$$\begin{aligned}
E &= \langle \hat{H} \rangle = \frac{1}{N} \sum_{i=1}^N \int \left[ \left( \frac{-1}{2} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right) \gamma_1(\mathbf{x}'_i; \mathbf{x}_i) \right]_{\mathbf{x}'_i = \mathbf{x}_i} d\mathbf{x}_i \\
&\quad + \frac{2}{N(N-1)} \sum_{i,j=1}^N \int \int \gamma_2(\mathbf{x}_i, \mathbf{x}_j; \mathbf{x}_i, \mathbf{x}_j) \frac{1}{r_{ij}} d\mathbf{x}_i d\mathbf{x}_j
\end{aligned}$$

i.e. if we knew  $\gamma_1(\mathbf{x}'_i; \mathbf{x}_i)$  and  $\gamma_2(\mathbf{x}_i, \mathbf{x}_j; \mathbf{x}_i, \mathbf{x}_j)$  then we would know the total energy, of course this is where all of many-body science sits. In fact if we knew  $\gamma_2(\mathbf{x}_i, \mathbf{x}_j; \mathbf{x}_i, \mathbf{x}_j)$  then from  $\gamma_1(\mathbf{x}'_1; \mathbf{x}_1) = \frac{2}{N-1} \int \gamma_2(\mathbf{x}'_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2$ , in principle, we could evaluate  $\gamma_1(\mathbf{x}'_1; \mathbf{x}_1)$ , and then we would be done, at least as far as the energy goes. So lets see if we can develop an intuition for what these reduced-density matrices means.

Lets simplify the above expression by extracting the spin degrees of freedom out of the above expressions. There is a very interesting discussion on N-representability on page 31-32 of Parr-Yang and also very interesting work by a number of people, in particular (in my opinion) the Mazziotti group in Chicago has done a lot of nice work on this. In any event to get rid of spins, one does the usual integration (sum will be written in the general form of an integral):

$$\begin{aligned}
\gamma_1(\mathbf{r}'_1 s_1; \mathbf{r}_1 s_1) &= N \int \cdots \int \Psi(\mathbf{r}'_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) \\
&\quad \times \Psi^*(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) d\mathbf{r}_2 ds_2 \dots d\mathbf{r}_N ds_N \\
\rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= \int \gamma_1(\mathbf{r}'_1 s_1; \mathbf{r}_1 s_1) ds_1 \\
&= N \int \cdots \int \Psi(\mathbf{r}'_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) \\
&\quad \times \Psi^*(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N) ds_1 d\mathbf{r}_2 ds_2 \dots d\mathbf{r}_N ds_N \\
\gamma_2(\mathbf{r}'_1 s_1, \mathbf{r}'_2 s_2; \mathbf{r}_1 s_1, \mathbf{r}_2 s_2) &= \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{r}'_1 s_1, \mathbf{r}'_2 s_2, \mathbf{r}_3 s_3, \dots, \mathbf{r}_N s_N) \\
&\quad \times \Psi^*(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \mathbf{r}_3 s_3, \dots, \mathbf{r}_N s_N) d\mathbf{r}_3 ds_3 \dots d\mathbf{r}_N ds_N \\
\rho_2(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) &= \int \int \gamma_2(\mathbf{r}'_1 s_1, \mathbf{r}'_2 s_2; \mathbf{r}_1 s_1, \mathbf{r}_2 s_2) ds_1 ds_2 \\
&= \frac{N(N-1)}{2} \int \cdots \int \Psi(\mathbf{r}'_1 s_1, \mathbf{r}'_2 s_2, \mathbf{r}_3 s_3, \dots, \mathbf{r}_N s_N) \\
&\quad \times \Psi^*(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \mathbf{r}_3 s_3, \dots, \mathbf{r}_N s_N) ds_1 ds_2 d\mathbf{r}_3 ds_3 \dots d\mathbf{r}_N ds_N
\end{aligned}$$

shorthand notation

$$\begin{aligned}\rho(\mathbf{r}_1) &= \rho_1(\mathbf{r}_1, \mathbf{r}_1) \\ &= N \int \cdots \int |\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)|^2 ds_1 d\mathbf{r}_2 ds_2 \dots d\mathbf{r}_N ds_N\end{aligned}$$

which is the electron density at  $\mathbf{r}_1$  and

$$\begin{aligned}\rho_2(\mathbf{r}_1, \mathbf{r}_2) &= \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{N(N-1)}{2} \int \cdots \int |\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \mathbf{r}_3 s_3, \dots, \mathbf{r}_N s_N)|^2 ds_1 ds_2 d\mathbf{r}_3 ds_3 \dots d\mathbf{r}_N ds_N\end{aligned}$$

and

$$\begin{aligned}\rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= \int \gamma_1(\mathbf{r}'_1 s_1; \mathbf{r}_1 s_1) ds_1 \\ &= \frac{2}{N-1} \int \int \gamma_2(\mathbf{r}'_1 s_1, \mathbf{r}_2 s_2; \mathbf{r}_1 s_1, \mathbf{r}_2 s_2) ds_2 ds_1 d\mathbf{r}_2 \\ \rho_1(\mathbf{r}'_1, \mathbf{r}_1) &= \frac{2}{N-1} \int \rho_2(\mathbf{r}'_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2\end{aligned}$$

in particular

$$\rho(\mathbf{r}_1) = \frac{2}{N-1} \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

The expectation of one and two particle operators can be evaluated similarly

...

$$\begin{aligned}E &= \frac{1}{N} \sum_{i=1}^N \int \left[ \left( \frac{-1}{2} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right) \gamma_1(\mathbf{r}'_i s_i; \mathbf{r}_i ds_i) \right]_{\mathbf{x}'_i = \mathbf{x}_i} d\mathbf{r}_i ds_i \\ &\quad + \frac{2}{N(N-1)} \sum_{i,j=1}^N \int \int \gamma_2(\mathbf{r}_i s_i, \mathbf{r}_j s_j; \mathbf{r}_i s_i, \mathbf{r}_j s_j) \frac{1}{r_{ij}} d\mathbf{r}_i ds_i d\mathbf{r}_j ds_j \\ &= \frac{1}{N} \sum_{i=1}^N \int \left( \frac{-1}{2} \nabla_i^2 \rho_1(\mathbf{r}'_i; \mathbf{r}_i) \right)_{\mathbf{r}'_i = \mathbf{r}_i} d\mathbf{r}_i + \frac{1}{N} \sum_{i=1}^N \int v_{ext}(\mathbf{r}_i) \rho(\mathbf{r}_i) d\mathbf{r}_i \\ &\quad + \frac{2}{N(N-1)} \sum_{i,j=1}^N \int \int \frac{1}{r_{ij}} \rho_2(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j\end{aligned}$$

again this doesn't seem to exactly match equation 2.4.9 of Parr-Yang, but I will push on, since it contains the same science. The first, second and third parts of the above equations correspond to the kinetic energy, the energy due to the



nuclei and the energy due to Coulomb potential. Lets examine components of the last piece

$$E_{ij}^{coulomb} = \int \int \frac{1}{r_{ij}} \rho_2(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j$$

if we only had classical Coulomb interaction between particles, e.g. Hartree limit, the above energy would be

$$J[\rho] = \frac{1}{2} \int \int \frac{1}{r_{ij}} \rho(\mathbf{r}_i) \rho(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j$$

where the factor 1/2 is due to double counting of interactions between particles. This suggests writing

$$\begin{aligned} \rho_2(\mathbf{r}_i, \mathbf{r}_j) &= \frac{1}{2} [\rho(\mathbf{r}_i) \rho(\mathbf{r}_j) + \rho(\mathbf{r}_i) \rho(\mathbf{r}_j) h(\mathbf{r}_i, \mathbf{r}_j)] \\ &= \frac{1}{2} \rho(\mathbf{r}_i) \rho(\mathbf{r}_j) [1 + h(\mathbf{r}_i, \mathbf{r}_j)] \end{aligned}$$

the *pair correlation function*  $h(\mathbf{r}_i, \mathbf{r}_j)$  is a function that incorporates *all non-classical effects* in the system, including exchange, i.e. the anti-symmetric property of the wavefunction (Fock's terms). It has very interesting and physically relevant properties.

Since  $\rho_2(\mathbf{r}_i, \mathbf{r}_j)$  is symmetric under exchange of the two particles,  $h(\mathbf{r}_i, \mathbf{r}_j)$  should be symmetric under exchange.

From

$$\begin{aligned} \rho(\mathbf{r}_1) &= \frac{2}{N-1} \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ &= \frac{\rho(\mathbf{r}_1)}{N-1} \int \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_2 \\ N-1 &= \int \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_2 \\ N-1 &= \int \rho(\mathbf{r}_2) d\mathbf{r}_2 + \int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\ &\quad \int \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1 \end{aligned}$$

which hold for all  $\mathbf{r}_1$ . It is conventional to define exchange-correlation hole (sometimes called the exchange-correlation charge) of an electron at  $\mathbf{r}_1$  by

$$\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2)$$

$$\begin{aligned}
\rho_2(\mathbf{r}_i, \mathbf{r}_j) &= \frac{1}{2}\rho(\mathbf{r}_i)\rho(\mathbf{r}_j) + \frac{1}{2}\rho(\mathbf{r}_i)\rho_{xc}(\mathbf{r}_i, \mathbf{r}_j) \\
&= \frac{1}{2}\rho(\mathbf{r}_i) [\rho(\mathbf{r}_j) + \rho_{xc}(\mathbf{r}_i, \mathbf{r}_j)]
\end{aligned}$$

then

$$\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$$

in trying to extract some "understanding" of all this, lets put  $\rho_2(\mathbf{r}_i, \mathbf{r}_j)$  back into the Coulomb energy

$$\begin{aligned}
E_{ij}^{coulomb} &= \int \int \frac{1}{r_{ij}} \rho_2(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \\
&= \frac{1}{2} \int \int \frac{1}{r_{ij}} \rho(\mathbf{r}_i) [\rho(\mathbf{r}_j) + \rho(\mathbf{r}_i)\rho_{xc}(\mathbf{r}_i, \mathbf{r}_j)] d\mathbf{r}_i d\mathbf{r}_j \\
&= \frac{1}{2} \int \int \frac{1}{r_{ij}} \rho(\mathbf{r}_i)\rho(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \\
&\quad + \frac{1}{2} \int \int \frac{1}{r_{ij}} \rho(\mathbf{r}_i)\rho_{xc}(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \\
&= J[\rho] + \frac{1}{2} \int \int \frac{1}{r_{ij}} \rho(\mathbf{r}_i)\rho_{xc}(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j
\end{aligned}$$

then one interprets the above equation as including the classical (Hartree) Coulomb piece plus a term that digs an exchange-correlation hole (that is why it is called density) that takes away from the Hartree energy. Note that condition  $\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$  means that one digs a charge, such that no matter how complicated the shape of the hole, it integrates to exactly -1, always! It is beautiful this comes out with no approximation and with so little effort. Of course, the challenge of what  $\rho_{xc}(\mathbf{r}_i, \mathbf{r}_j)$  (which is a non-local function) remains and gives us jobs.

## 4 Hartree-Fock in the density matrix language

If we take the state of the system to be a single determinant as is the case in Hartree-Fock theory

$$\begin{aligned}
\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \dots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \dots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \dots & \dots & \psi_N(\mathbf{x}_N) \end{vmatrix} \\
&= \frac{1}{\sqrt{N!}} \det(\psi_1 \psi_2 \dots \psi_N).
\end{aligned}$$

Parr-Yang (page-34) has a very nice discussion and derivation of the following

and theorems about uniqueness of the form of the reduced-density matrices in the Hartree-Fock limit

$$\begin{aligned}
\gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) &= \sum_{i=1}^N \psi_i(\mathbf{x}'_1) \psi_i^*(\mathbf{x}_1) \\
\gamma_2^{HF}(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{2} \begin{vmatrix} \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) & \gamma_1^{HF}(\mathbf{x}'_2; \mathbf{x}_1) \\ \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_2) & \gamma_1^{HF}(\mathbf{x}'_2; \mathbf{x}_2) \end{vmatrix} \\
\gamma_p^{HF}(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_p; \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_p) &= \frac{1}{2} \begin{vmatrix} \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) & \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_2) & \dots & \dots & \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_p) \\ \gamma_1^{HF}(\mathbf{x}'_2; \mathbf{x}_1) & \gamma_1^{HF}(\mathbf{x}'_2; \mathbf{x}_2) & \dots & \dots & \gamma_1^{HF}(\mathbf{x}'_2; \mathbf{x}_p) \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ \gamma_1^{HF}(\mathbf{x}'_p; \mathbf{x}_1) & \vdots & \dots & \dots & \gamma_1^{HF}(\mathbf{x}'_p; \mathbf{x}_p) \end{vmatrix}
\end{aligned}$$

going back to the previous section where I wrote the total energy in terms of reduced-density matrices (and reverting to Parr-Yang notation, equation 2.3.37)

$$\begin{aligned}
E &= \int \left[ \left( \frac{-1}{2} \nabla_1^2 + v_{ext}(\mathbf{r}_1) \right) \gamma_1(\mathbf{x}'_1; \mathbf{x}_1) \right]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 \\
&\quad + \int \int \gamma_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) \frac{1}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2
\end{aligned}$$

which in the Hartree-Fock approximation is then (for even number of particles, "closed shell"), using

$$\gamma_2^{HF}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2} [\gamma_1^{HF}(\mathbf{x}_1; \mathbf{x}_1) \gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_2) - \gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_1) \gamma_1^{HF}(\mathbf{x}_1; \mathbf{x}_2)]$$

$$\begin{aligned}
E_{HF} &= \int \left[ \left( \frac{-1}{2} \nabla_1^2 + v_{ext}(\mathbf{r}_1) \right) \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) \right]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 \\
&\quad + \frac{1}{2} \int \int [\gamma_1^{HF}(\mathbf{x}_1; \mathbf{x}_1) \gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_2) - \gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_1) \gamma_1^{HF}(\mathbf{x}_1; \mathbf{x}_2)] \frac{1}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\
&= \int \left[ \left( \frac{-1}{2} \nabla_1^2 + v_{ext}(\mathbf{r}_1) \right) \gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) \right]_{\mathbf{x}'_1 = \mathbf{x}_1} d\mathbf{x}_1 \\
&\quad + \frac{1}{2} \int \int \gamma_1^{HF}(\mathbf{x}_1; \mathbf{x}_1) \gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_2) \frac{1}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 - \frac{1}{2} \int \int |\gamma_1^{HF}(\mathbf{x}_2; \mathbf{x}_1)|^2 \frac{1}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2
\end{aligned}$$

which would then be minimized with respect to the wavefunctions, i.e. with respect to  $\gamma_1^{HF}(\mathbf{x}'_1; \mathbf{x}_1) = \sum_{i=1}^N \psi_i(\mathbf{x}'_1) \psi_i^*(\mathbf{x}_1)$  to give us back the usual Hartree-Fock equations (for even number of particles, "closed shell", pages 38-40 of Parr-Yang).

$$\begin{aligned}
E_{HF}[\rho_1] &= T[\rho_1] + v_{ext}[\rho] + J[\rho] - K[\rho_1] \\
T[\rho_1] &= \int \left[ \left( \frac{-1}{2} \nabla_1^2 + v_{ext}(\mathbf{r}_1) \right) \rho_1^{HF}(\mathbf{r}'_1, \mathbf{r}_1) \right]_{\mathbf{r}'_1 = \mathbf{r}_1} d\mathbf{r}_1 \\
v_{ext}[\rho] &= \int v_{ext}(\mathbf{r}) \rho^{HF}(\mathbf{r}) d\mathbf{r} \\
J[\rho] &= \frac{1}{2} \int \int \rho_1^{HF}(\mathbf{r}_1) \rho_1^{HF}(\mathbf{r}_2) \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
K[\rho_1] &= \frac{1}{4} \int \int |\rho_1^{HF}(\mathbf{r}_1, \mathbf{r}_2)|^2 \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2
\end{aligned}$$

defining the pair correlation function  $h^{HF}(\mathbf{r}_i, \mathbf{r}_j)$  in the Hartree-Fock limit (using the notation of the last section):

$$\begin{aligned}
\rho_{xc}^{HF}(\mathbf{r}_1, \mathbf{r}_2) &= \rho_x^{HF}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2} \frac{|\rho_1^{HF}(\mathbf{r}_2, \mathbf{r}_1)|^2}{\rho^{HF}(\mathbf{r}_2)} \\
h^{HF}(\mathbf{r}_1, \mathbf{r}_2) &= -\frac{1}{4} \frac{|\rho_1^{HF}(\mathbf{r}_2, \mathbf{r}_1)|^2}{\rho^{HF}(\mathbf{r}_1) \rho^{HF}(\mathbf{r}_2)}
\end{aligned}$$

note that the summation rules hold in the Hartree-Fock limit:

$$\begin{aligned}
\rho^{HF}(\mathbf{r}_1) &= \frac{2}{N-1} \int \rho_2^{HF}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \\
&= \frac{\rho^{HF}(\mathbf{r}_1)}{N-1} \int \rho^{HF}(\mathbf{r}_2) [1 + h^{HF}(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_2 \\
N-1 &= \int \rho^{HF}(\mathbf{r}_2) [1 + h^{HDF}(\mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_2 \\
\int \rho^{HF}(\mathbf{r}_2) h^{HF}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int \rho_x^{HF}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1.
\end{aligned}$$

- 1) Density-Functional Theory of Atoms and Molecules, by R.C. Parr and W. Yang.
- 2) Modern Quantum Chemistry, A. Szabo and N. S. Ostlund.
- 3) Modern Quantum Mechanics, J. J. Sakurai.