Problem set 2
FYS4480

Tentative answers to the second set

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In these exercises we will mostly be using *second quantization*-notation. We won't go into to much details about the notation, so for further reference see either the lecutre notes or chapter 3 in Shavitt and Bartlett.

Exercise 3

In this exercise, we are looking at a general N-particle Slater determinant, which we will denote $|SD\rangle$. We also look at three other N-particle SDs, that have one, two and three noncoincidence with the first SD, meaning they have certain single-particle states replaced by others. The notation we use to denote this is as follows, the state $|SD\rangle_i^j$ has had the single-particle state ϕ_i replaced by ϕ_j—this of course assumes that ϕ_j was not a part of the original SD. Throughout these exercises, we will use the fact that these SDs form an orthonormal set, in the sense that

$$
\begin{aligned}
\langle SD|SD\rangle &= 1, \\
\langle SD|SD_i^j\rangle &= 0, \\
\langle SD_i^j|SD_i^j\rangle &= 1,
\end{aligned}
$$

and so on.

We will look at the matrix elements of general onebody and twobody operators represented in the basis of these SDs. The operators are as usual

$$\hat{F} = \sum_i \hat{f}(x_i), \qquad \hat{G} = \sum_{i<j} \hat{g}(x_i, x_j).$$

which in second quantization can be written as

$$
\begin{aligned}
\hat{F} &= \sum_{\alpha,\beta} \langle\alpha|\hat{f}|\beta\rangle a_\alpha^\dagger a_\beta, \\
\hat{G} &= \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \langle\alpha\beta|\hat{g}|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma.
\end{aligned}
$$

a)

We start by simply looking at the expectation values of $|SD\rangle$ for the onebody and twobody operators.

Onebody operator

When we insert the onebody operator, we see that only the terms where $\alpha = \beta$ survive and we are left with N contributions to the expectation value

$$\begin{aligned}\langle SD|\hat{F}|SD\rangle &= \sum_{\alpha,\beta} \langle\alpha|\hat{f}|\beta\rangle\langle SD|a_\alpha^\dagger a_\beta|SD\rangle \\ &= \sum_{\alpha} \langle\alpha|\hat{f}|\alpha\rangle.\end{aligned}$$

Twobody operator

When inserting the twobody operator, we have

$$\langle SD|\hat{F}|SD\rangle = \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta} \langle\alpha\beta|\hat{g}|\gamma\delta\rangle\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma|SD\rangle.$$

We can firste note that any term where $\alpha = \beta$ or $\gamma = \delta$ vanish, because

$$\hat{a}_\alpha^\dagger \hat{a}_\alpha^\dagger |SD\rangle = 0 \quad \text{and} \quad \hat{a}_\alpha \hat{a}_\alpha |SD\rangle = 0.$$

Next we note that to get any contribution, we must add the same states back that we annihilate, meaning either $\alpha = \gamma$ and $\beta = \delta$ or vice versa. We then have

$$\begin{aligned}\langle SD|\hat{F}|SD\rangle = \frac{1}{2}\sum_{\alpha,\beta} \Big(&\langle\alpha\beta|\hat{g}|\alpha\beta\rangle\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\alpha|SD\rangle \\ &+ \langle\alpha\beta|\hat{g}|\beta\alpha\rangle\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\alpha a_\beta|SD\rangle\Big).\end{aligned}$$

To simplify further, we use the anticommutation relations:

$$\hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger = -\hat{a}_\beta^\dagger \hat{a}_\alpha^\dagger, \quad \hat{a}_\alpha \hat{a}_\beta = -\hat{a}_\beta \hat{a}_\alpha, \qquad \hat{a}_\alpha^\dagger \hat{a}_\beta = \delta_{\alpha\beta} - \hat{a}_\beta \hat{a}_\alpha^\dagger,$$

and also the number operator

$$\hat{a}_\alpha^\dagger \hat{a}_\alpha = \hat{n}_\alpha,$$

we find that

$$\begin{aligned}\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\beta a_\alpha|SD\rangle &= \langle SD|a_\alpha^\dagger a_\alpha a_\beta^\dagger a_\beta|SD\rangle = \langle SD|\hat{n}_\alpha \hat{n}_\beta|SD\rangle = 1 \\ \langle SD|a_\alpha^\dagger a_\beta^\dagger a_\alpha a_\beta|SD\rangle &= -\langle SD|a_\alpha^\dagger a_\alpha a_\beta^\dagger a_\beta|SD\rangle = -\langle SD|\hat{n}_\alpha \hat{n}_\beta|SD\rangle = -1.\end{aligned}$$

Combining these results gives

$$\langle SD|\hat{G}|SD\rangle = \frac{1}{2}\sum_{\alpha,\beta} \Big(\langle\alpha\beta|\hat{g}|\alpha\beta\rangle - \langle\alpha\beta|\hat{g}|\beta\alpha\rangle\Big).$$

We recognize the *Hartree* and *Fock* terms respectively. Note that all terms where $\alpha = \beta$ will vanish, as expected.

b)

We now look at the cross terms where there is one noncoincidence between the SDs, i.e., $|SD\rangle$ and $|SD_i^j\rangle$.

Onebody operator

When we insert the onebody operator, we get

$$\langle SD|\hat{F}|SD_i^j\rangle = \sum_{\alpha,\beta}\langle\alpha|\hat{f}|\beta\rangle\langle SD|a_\alpha^\dagger a_\beta|SD_i^j\rangle.$$

As $|SD_i^j\rangle$ has had its ϕ_i state replaced with ϕ_j, we know that

$$\hat{a}_i^\dagger \hat{a}_j|SD_i^j\rangle = |SD\rangle.$$

For all other combinations of α and β, the noncoincidence makes the integral vanish, so we are left with only one contribution

$$\langle SD|\hat{F}|SD_i^j\rangle = \langle i|\hat{f}|j\rangle.$$

Twobody operator

For the twobody operator, we have the expression

$$\langle SD|\hat{G}|SD_i^j\rangle = \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|\hat{g}|\gamma\delta\rangle\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma|SD_i^j\rangle.$$

For any term to contribute to the final sum the noncoincidence must be removed, this means we can reduce the sum over all four indices to a single sum as follows

$$\begin{aligned}\langle SD|\hat{G}|SD_i^j\rangle = \frac{1}{2}\sum_{\alpha}\big[&\langle\alpha i|\hat{g}|\alpha j\rangle\langle SD|a_\alpha^\dagger a_i^\dagger a_j a_\alpha|SD_i^j\rangle \\ &+ \langle\alpha i|\hat{g}|j\alpha\rangle\langle SD|a_\alpha^\dagger a_i^\dagger a_\alpha a_j|SD_i^j\rangle \\ &+ \langle i\alpha|\hat{g}|\alpha j\rangle\langle SD|a_i^\dagger a_\alpha^\dagger a_j a_\alpha|SD_i^j\rangle \\ &+ \langle i\alpha|\hat{g}|j\alpha\rangle\langle SD|a_i^\dagger a_\alpha^\dagger a_\alpha a_j|SD_i^j\rangle\big].\end{aligned}$$

Unlike the previous exercise, where there were only two terms, we now have four terms. However, we can simplify these by using the fact that generally $\langle\alpha\beta|\hat{q}|\gamma\delta\rangle = \langle\beta\alpha|\hat{q}|\delta\gamma\rangle$. Combining this with the anticommutation relations, we find that

$$\langle SD|\hat{G}|SD_i^j\rangle = \sum_{\alpha}\Big(\langle\alpha i|\hat{g}|\alpha j\rangle - \langle\alpha i|\hat{g}|j\alpha\rangle\Big).$$

c)

We now look at the cross term where there are two noncoincidences between the SDs, i.e., $|SD\rangle$ and $|SD_{ij}^{kl}\rangle$.

Onebody operator

Again we start with the definition of the onebody operator

$$\langle SD|\hat{F}|SD_{ij}^{kl}\rangle = \sum_{\alpha,\beta}\langle\alpha|\hat{f}|\beta\rangle\langle SD|a_\alpha^\dagger a_\beta|SD_{ij}^{kl}\rangle.$$

We see that for all α and β, there will always be at least one noncoincidence between the SDs, and all terms vanish. We simply end up with

$$\langle SD|\hat{F}|SD_{ij}^{kl}\rangle = 0.$$

Twobody operator

From the definition of the twobody operator we have

$$\langle SD|\hat{G}|SD_{ij}^{kl}\rangle = \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|\hat{g}|\gamma\delta\rangle\langle SD|a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma|SD_{ij}^{kl}\rangle.$$

We see that only the terms where the ϕ_k and ϕ_l states are annhilated and the states $\phi_i\phi_j$ are constructed contribute, so we have

$$\begin{aligned}\langle SD|\hat{G}|SD_{ij}^{kl}\rangle = \frac{1}{2}\big[&\langle ij|\hat{g}|kl\rangle\langle SD|a_i^\dagger a_j^\dagger a_k a_l|SD_{ij}^{kl}\rangle \\ &+ \langle ij|\hat{g}|lk\rangle\langle SD|a_i^\dagger a_j^\dagger a_k a_l|SD_{ij}^{kl}\rangle \\ &+ \langle ji|\hat{g}|kl\rangle\langle SD|a_j^\dagger a_i^\dagger a_l a_k|SD_{ij}^{kl}\rangle \\ &+ \langle ji|\hat{g}|lk\rangle\langle SD|a_j^\dagger a_i^\dagger a_k a_l|SD_{ij}^{kl}\rangle\big].\end{aligned}$$

And we see that again we get four terms. Using the same simplifications we used in the previous exercise, we find

$$\langle SD|\hat{G}|SD_{ij}^{kl}\rangle = \langle ij|\hat{g}|kl\rangle - \langle ij|\hat{g}|lk\rangle$$

More than two noncoincidences

We can now ask ourselves what the matrix elements would be if there were three or more noncoincidences between the SDs, e.g., $\langle SD|\hat{G}|SD_{ijk}^{lmn}\rangle$.

Let us look closer at our results so far. When there were no noncoincidences, the onebody operator had N terms, one for each particle, and the twobody operator had $N^2/2$ terms[1], one for each pair of particles. When we introduced one noncoincidence, the onbody operator matrix elements reduced to having

[1] Technically, there are $(N-1)^2$ terms in the sum, as each pair of particles actually contribute twice, once with their direct term, and one for their exchange term. Yet no particle forms a pair with themselves. However, in this discussion let us lump the exchange and direct terms together as one.

only one term, the one for the differing single-particle state. Similarily, the twobody operator reducing to having only N terms, one for each particle-pair including the differening states as one of the particles. When we looked at two noncoincidence, the onebody operator vanished completely and the twodbody operator was left with only a single term—the interaction between the two non-matching states.

From this development, it is apparent that the matrix elements for both operators vanish when there are three or more noncoincidences. Likewise we would expect the matrix elements of a three-body operator to consist of a single term[2] for a three noncoincidence case and vanish for four or more noncoincidences.

Excercise 4

The density of particles with coordinates $\boldsymbol{x}$ is given by

$$n(\boldsymbol{x}) = N \int \left|\Psi_{\mathrm{AS}}(\boldsymbol{x}, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\right|^2 \,\mathrm{d}\boldsymbol{x}_2 \mathrm{d}\boldsymbol{x}_3 \cdots \boldsymbol{x}_N.$$

Writing out the SD for $N = 2$ we have

$$\begin{aligned} n(\boldsymbol{x}) = 2 \int & \left[\frac{1}{\sqrt{2}} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_1(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_1)\right]^* \\ & \qquad \left[\frac{1}{\sqrt{2}} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_1(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_1)\right] \mathrm{d}\boldsymbol{x}_2 \\ = {} & \psi_1^* \psi_1 + \psi_2^* \psi_2 = |\psi_1|^2 + |\psi_2|^2. \end{aligned}$$

So we see that the cross terms vanish due to the orthonormality of the single-particle states. We see that when we scale to a larger N this will always be the case. We then have the general result

$$n(\boldsymbol{x}) = N \int \left|\Psi_{\mathrm{AS}}(\boldsymbol{x}, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)\right|^2 \,\mathrm{d}\boldsymbol{x}_2 \mathrm{d}\boldsymbol{x}_3 \cdots \boldsymbol{x}_N = \sum_k |\psi_k|^2.$$

Which is what we wanted to show. However, when writing this out with the antisymmetrizer operator, the result is different. See the end of this document for a better explanation of this problem.

b)

We now want to calculate the matrix elements

$$\langle \alpha_1 \alpha_2 | \hat{F} | \alpha_1 \alpha_2 \rangle \quad \text{and} \quad \langle \alpha_1 \alpha_2 | \hat{G} | \alpha_1 \alpha_2 \rangle.$$

Where $|\alpha_1 \alpha_2\rangle = a^\dagger_{\alpha_1} a^\dagger_{\alpha_2} |0\rangle$. We will do this in second quantization, and use our general results from exercise 3a.

[2] Again we are lumping all exchange terms that might arise into one.

Onebody operator

For the onebody operator, we found that

$$\langle SD|\hat{F}|SD\rangle = \sum_{\alpha} \langle \alpha|\hat{f}|\alpha\rangle,$$

so inserting our Slater determinant gives

$$\langle \alpha_1\alpha_2|\hat{F}|\alpha_1\alpha_2\rangle = \langle \alpha_1|\hat{f}|\alpha_1\rangle + \langle \alpha_2|\hat{f}|\alpha_2\rangle.$$

Twobody operator

For the twobody operator, we found the general result

$$\langle SD|\hat{G}|SD\rangle = \frac{1}{2}\sum_{\alpha,\beta}\Big(\langle \alpha\beta|\hat{g}|\alpha\beta\rangle - \langle \alpha\beta|\hat{g}|\beta\alpha\rangle\Big).$$

So in this case, we have

$$\langle \alpha_1\alpha_2|\hat{G}|\alpha_1\alpha_2\rangle = \frac{1}{2}\Big(\langle \alpha_1\alpha_2|\hat{g}|\alpha_1\alpha_2\rangle - \langle \alpha_1\alpha_2|\hat{g}|\alpha_2\alpha_1\rangle + \langle \alpha_2\alpha_1|\hat{g}|\alpha_2\alpha_1\rangle - \langle \alpha_2\alpha_1|\hat{g}|\alpha_1\alpha_2\rangle\Big).$$

Using the fact that generally $\langle \alpha\beta|\hat{q}|\gamma\delta\rangle = \langle \beta\alpha|\hat{q}|\delta\gamma\rangle$, we can rewrite this to

$$\langle \alpha_1\alpha_2|\hat{G}|\alpha_1\alpha_2\rangle = \langle \alpha_1\alpha_2|\hat{g}|\alpha_1\alpha_2\rangle - \langle \alpha_1\alpha_2|\hat{g}|\alpha_2\alpha_1\rangle = \langle \alpha_1\alpha_2|\hat{g}|\alpha_1\alpha_2\rangle_{\mathrm{AS}}.$$

What is going on?

We have the definition

$$n(x) = N\int |\Psi_{\mathrm{AS}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|^2 \,\mathrm{d}\boldsymbol{x}_2\cdots\mathrm{d}\boldsymbol{x}_N,$$

and want to show that this is equivalent to

$$n(x) = \sum_k |\psi_k|^2.$$

If we calculate $n(x)$ explicitly for the $n = 2$ and $n = 3$ cases by inserting the complete expression for the Slater determinants, we get the right answer. Let us for example look at $N = 2$:

$$\begin{aligned}
n(\boldsymbol{x}) = 2 \int \bigg[\frac{1}{\sqrt{2}} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_1(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_1) \bigg]^* \\
\bigg[\frac{1}{\sqrt{2}} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) - \psi_1(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_1) \bigg] \, \mathrm{d}\boldsymbol{x}_2 \\
&= \int \psi_1^*(x_1)\psi_2^*(x_2)\psi_1(x_1)\psi_2(x_2) \, \mathrm{d}\boldsymbol{x}_2 \\
&\quad - \int \psi_1^*(x_1)\psi_2(x_1)\psi_2^*(x_2)\psi_1(x_2) \, \mathrm{d}\boldsymbol{x}_2 \\
&\quad - \int \psi_2^*(x_1)\psi_1(x_1)\psi_1^*(x_2)\psi_2(x_2) \, \mathrm{d}\boldsymbol{x}_2 \\
&\quad + \int \psi_2^*(x_1)\psi_2(x_1)\psi_1^*(x_2)\psi_1(x_2) \, \mathrm{d}\boldsymbol{x}_2 \\
&= \psi_1^*\psi_1 + \psi_2^*\psi_2 = |\psi_1|^2 + |\psi_2|^2.
\end{aligned}$$

If however, we instead use the asymmetrizer to express the Slater determinant

$$\Psi_{\mathrm{AS}} = \sqrt{N!}\mathcal{A}\phi_H.$$

We can simplify the probability density as follows

$$|\Psi_{AS}|^2 = N!(\mathcal{A}\phi_H)^*(\mathcal{A}\phi_H) = N!\phi_H^*\mathcal{A}^*\mathcal{A}\phi_H = N!\phi_H^*\mathcal{A}\phi_H.$$

Where we have used $\mathcal{A}^*\mathcal{A} = \mathcal{A}^2 = \mathcal{A}$. Inserting this into the original defintion gives us

$$\begin{aligned}
n(x) &= N \int |\Psi_{\mathrm{AS}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)|^2 \, \mathrm{d}\boldsymbol{x}_2 \cdots \mathrm{d}\boldsymbol{x}_N \\
&= NN! \int \phi_H^*\mathcal{A}\phi_H \, \mathrm{d}\boldsymbol{x}_2 \cdots \mathrm{d}\boldsymbol{x}_N,
\end{aligned}$$

And inserting the definition of the asymmetrizer gives

$$n(x) = N \sum_p (-)^p \int \phi_H^* \hat{P} \phi_H \, \mathrm{d}\boldsymbol{x}_2 \cdots \mathrm{d}\boldsymbol{x}_N$$

But any permutation of the second Hartree-function will make the integral vanish, so we have

$$n(x) = N \int \phi_H^*\phi_H \, \mathrm{d}\boldsymbol{x}_2 \cdots \mathrm{d}\boldsymbol{x}_N = N|\psi_1|^2$$

The problem here is that we get two different results, as generally $|\psi_1|^2 + |\psi_2|^2 \neq 2|\psi_1|^2$. In the case where $|\psi_1|^2 = |\psi_2|^2$ however, the answers match.

If we instead use the defintion

$$n(x) = \sum_i \int |\Psi_{\mathrm{AS}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \, \mathrm{d}\boldsymbol{x}_{\mathbf{1}} \ldots \mathrm{d}\boldsymbol{x}_{i-1}\mathrm{d}\boldsymbol{x}_{i+1} \cdots \mathrm{d}\boldsymbol{x}_N.$$

Meaning we integrate over every coordinate except for one in turn, and then add the results back together. Then both results will match. However, both defintions of the density *should* be equal, as changing pairs of coordinates only means changing particles, which shouldn't make any physical difference, as they are indistinguishable. In fact we know that $|\hat{P}\Psi|^2 = |\Psi|^2$ for any state! So there definitly should not be any difference.

The error might be in

$$|\Psi_{AS}|^2 = N!(\mathcal{A}\phi_H)^*(\mathcal{A}\phi_H) = N!\phi_H^*\mathcal{A}^*\mathcal{A}\phi_H = N!\phi_H^*\mathcal{A}\phi_H.$$

But it is not readily apparant why this is wrong, as $\mathcal{A}^\dagger = \mathcal{A}$, and $\mathcal{A}^2 = 2$.