Second Midterm Project
FYS-KJM4480

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Exercise 1)

Show that $\hat{H}_0$ and V commute with $\hat{S}_z$ and $\hat{S}^2$.

$$\hat{H}_0 := \xi \sum_{p\sigma} (p-1)a^\dagger_{p\sigma}a_{p\sigma},$$

$$\hat{V} := -\frac{1}{2}g \sum_{pq} a^\dagger_{p+}a^\dagger_{p-}a_{q-}a_{q+},$$

$$\hat{S}_z := \frac{1}{2}\sum_{p\sigma} \sigma a^\dagger_{p\sigma}a_{p\sigma},$$

$$\hat{S}^2 := \hat{S}^2_z + \frac{1}{2}\left(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+\right),$$

$$\hat{S}_\pm := \sum_p a^\dagger_{p\pm}a_{p\mp}.$$

Anti-commutation relations

$$\{\hat{a}^\dagger_\alpha, \hat{a}^\dagger_\beta\} = \{\hat{a}_\alpha, \hat{a}_\beta\} = 0, \qquad \{\hat{a}^\dagger_\alpha, \hat{a}_\beta\} = \delta_{\alpha\beta},$$

The commutator $[\hat{H}_0, \hat{S}_z]$

We start by inserting the operators in the definition

$$[\hat{H}_0, \hat{S}_z] = \hat{H}_0\hat{S}_z - \hat{S}_z\hat{H}_0$$

$$= \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\left(a^\dagger_{p\sigma}a_{p\sigma}a^\dagger_{q\lambda}a_{q\lambda} - a^\dagger_{q\lambda}a_{q\lambda}a^\dagger_{p\sigma}a_{p\sigma}\right).$$

We now swap the two middle operators in the second term, this gives a delta-term

$$[\hat{H}_0, \hat{S}_z] = \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\left(a^\dagger_{p\sigma}a_{p\sigma}a^\dagger_{q\lambda}a_{q\lambda} - a^\dagger_{q\lambda}(\delta_{pq}\delta_{\sigma\lambda} - a^\dagger_{p\sigma}a_{q\lambda})a_{p\sigma}\right)$$

$$= \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\left(a^\dagger_{p\sigma}a_{p\sigma}a^\dagger_{q\lambda}a_{q\lambda} + a^\dagger_{q\lambda}a^\dagger_{p\sigma}a_{q\lambda}a_{p\sigma} - \delta_{pq}\delta_{\sigma\lambda}a^\dagger_{q\lambda}a_{p\sigma}\right).$$

We now swap the first and second, and third and fourth operator in the second term. We get no delta-terms, and we have no total change in sign

$$[\hat{H}_0, \hat{S}_z] = \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\left(a^\dagger_{p\sigma}a_{p\sigma}a^\dagger_{q\lambda}a_{q\lambda} + a^\dagger_{p\sigma}a^\dagger_{q\lambda}a_{p\sigma}a_{q\lambda} - \delta_{pq}\delta_{\sigma\lambda}a^\dagger_{q\lambda}a_{p\sigma}\right).$$

Again we swap the two middle operators, getting another delta term

$$[\hat{H}_0, \hat{S}_z] = \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\left(a^\dagger_{p\sigma}a_{p\sigma}a^\dagger_{q\lambda}a_{q\lambda} + a^\dagger_{p\sigma}(\delta_{pq}\delta_{\lambda\sigma} - a_{p\sigma}a^\dagger_{q\lambda})a_{q\lambda} - \delta_{pq}\delta_{\sigma\lambda}a^\dagger_{q\lambda}a_{p\sigma}\right)$$

$$= \frac{\xi}{2}\sum_{pq\sigma\lambda} \lambda(p-1)\delta_{pq}\delta_{\lambda\sigma}\left(a^\dagger_{p\sigma}a_{q\lambda} - a^\dagger_{q\lambda}a_{p\sigma}\right).$$

Due to the Kronecker-deltas the only surviving terms in the sums will have $p = q$ and $\sigma = \lambda$, meaning the two terms will cancel out, so we have

$$[\hat{H}_0, \hat{S}_z] = 0,$$

and we have confirmed that $\hat{H}_0$ and $\hat{S}_z$ commute.

The commutator $[\hat{V}, \hat{S}_z]$

Again, we start from the definition

$$[\hat{V}, \hat{S}_z] = \hat{V}\hat{S}_z - \hat{S}_z\hat{V}$$
$$= \frac{g}{4}\sum_{pqr\sigma}\sigma\left(a_{r\sigma}^\dagger a_{r\sigma}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+} - a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}a_{r\sigma}^\dagger a_{r\sigma}\right).$$

We now move the $a_{r\sigma}^\dagger$-operator in the second term to the front by succesively swapping it to the left

$$a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}a_{r\sigma}^\dagger a_{r\sigma}$$
$$= a_{p+}^\dagger a_{p-}^\dagger a_{q-}\left(\delta_{qr}\delta_{\sigma+} - a_{r\sigma}^\dagger a_{q+}\right)a_{r\sigma}$$
$$= \delta_{qr}\delta_{\sigma+}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{r\sigma} - a_{p+}^\dagger a_{p-}^\dagger\left(\delta_{qr}\delta_{\sigma-} - a_{r\sigma}^\dagger a_{q-}\right)a_{q+}a_{r\sigma}$$
$$= \delta_{qr}\delta_{\sigma+}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{r\sigma} - \delta_{qr}\delta_{\sigma-}a_{p+}^\dagger a_{p-}^\dagger a_{q+}a_{r\sigma} + a_{r\sigma}^\dagger a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}a_{r\sigma}.$$

In the final term here, we now move the $a_{r\sigma}$ by successive shifts

$$a_{r\sigma}^\dagger a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}a_{r\sigma}$$
$$= a_{r\sigma}^\dagger a_{p+}^\dagger\left(\delta_{pr}\delta_{\sigma-} - a_{r\sigma}a_{p-}^\dagger\right)a_{q-}a_{q+}$$
$$= \delta_{pr}\delta_{\sigma-}a_{r\sigma}^\dagger a_{p+}^\dagger a_{q-}a_{q+} - a_{r\sigma}^\dagger\left(\delta_{pr}\delta_{\sigma+} - a_{r\sigma}a_{p+}^\dagger\right)a_{p-}^\dagger a_{q-}a_{q+}$$
$$= \delta_{pr}\delta_{\sigma-}a_{r\sigma}^\dagger a_{p+}^\dagger a_{q-}a_{q+} - \delta_{pr}\delta_{\sigma+}a_{r\sigma}^\dagger a_{p-}^\dagger a_{q-}a_{q+} + a_{r\sigma}^\dagger a_{r\sigma}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}.$$

Putting this result back into the original expression gives

$$[\hat{V}, \hat{S}_z] = \frac{g}{4}\sum_{pqr\sigma}\sigma\big(\delta_{pr}\delta_{\sigma+}a_{r\sigma}^\dagger a_{p-}^\dagger a_{q-}a_{q+} + \delta_{qr}\delta_{\sigma-}a_{p+}^\dagger a_{p-}^\dagger a_{q+}a_{r\sigma}$$
$$- \delta_{qr}\delta_{\sigma+}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{r\sigma} - \delta_{pr}\delta_{\sigma-}a_{r\sigma}^\dagger a_{p+}^\dagger a_{q-}a_{q+}\big).$$

We now perform the sum over σ, giving

$$[\hat{V}, \hat{S}_z] = \frac{g}{4}\sum_{pqr}\delta_{pr}\big(a_{r+}^\dagger a_{p-}^\dagger a_{q-}a_{q+} + a_{r-}^\dagger a_{p+}^\dagger a_{q-}a_{q+}\big)$$
$$- \delta_{qr}\big(a_{p+}^\dagger a_{p-}^\dagger a_{q+}a_{r-} + a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{r+}\big).$$

We now perform the sum over p and q, we see the only surviving terms are those were $p = r$ or $q = r$, giving

$$[\hat{V}, \hat{S}_z] = \frac{g}{4}\sum_{r}\big(a_{r+}^\dagger a_{r-}^\dagger a_{r-}a_{r+} + a_{r-}^\dagger a_{r+}^\dagger a_{r-}a_{r+} - a_{r+}^\dagger a_{r-}^\dagger a_{r+}a_{r-} - a_{r+}^\dagger a_{r-}^\dagger a_{r-}a_{r+}\big).$$

We see that the terms cancel each other out, leaving

$$[\hat{V}, \hat{S}_z] = 0,$$

and we have confirmed that $\hat{V}$ and $\hat{S}_z$ commute.

The commutator $[\hat{H}_0, \hat{S}_\pm]$

From the definition, we have

$$
\begin{aligned}
[\hat{H}_0, \hat{S}_\pm] &= \hat{H}_0 \hat{S}_\pm - \hat{S}_\pm \hat{H}_0 \\
&= \xi \sum_{pq\sigma} (p-1) \left(a_{p\sigma}^\dagger a_{p\sigma} a_{q\pm}^\dagger a_{q\mp} - a_{q\pm}^\dagger a_{q\mp} a_{p\sigma}^\dagger a_{p\sigma} \right).
\end{aligned}
$$

Again, we shift the operators around in the second term around, so that it cancels with the first term, we get the following result

$$
[\hat{H}_0, \hat{S}_\pm] = \xi \sum_{pq\sigma} (p-1) \delta_{pq} (\delta_{\sigma\pm} - \delta_{\sigma\mp}).
$$

We can now take the sum over σ, which makes the entire commutator vanish, as the two Kronecker-delta's with σ cancel each other out, so we have

$$
[\hat{H}_0, \hat{S}_\pm] = 0.
$$

And $\hat{H}_0$ commutes with $\hat{S}_\pm$.

The commutator $[\hat{V}, \hat{S}_\pm]$

From the definition, we have

$$
\begin{aligned}
[\hat{V}, \hat{S}_\pm] &= \hat{V} \hat{S}_\pm - \hat{S}_\pm \hat{V} \\
&= -\frac{g}{2} \sum_{pqr} a_{p+}^\dagger a_{p-}^\dagger a_{q-} a_{q+} a_{r\pm}^\dagger a_{r\mp} - a_{r\pm}^\dagger a_{r\mp} a_{p+}^\dagger a_{p-}^\dagger a_{q-} a_{q+}.
\end{aligned}
$$

Shifting the operators around in the second term makes it cancel with the first, but shifting the operators generates some terms, we have

$$
\begin{aligned}
[\hat{V}, \hat{S}_\pm] &= \hat{V} \hat{S}_\pm - \hat{S}_\pm \hat{V} \\
&= \frac{g}{2} \sum_{pqr} \big(\delta_{pr} \delta_{\mp+} a_{r\pm}^\dagger a_{p-}^\dagger a_{q-} a_{q+} - \delta_{pr} \delta_{\mp-} a_{r\pm}^\dagger a_{p+}^\dagger a_{q-} a_{q+} \\
&\qquad + \delta_{qr} \delta_{\pm-} a_{p+}^\dagger a_{p-}^\dagger a_{q+} a_{r\mp} - \delta_{qr} \delta_{\pm+} a_{p+}^\dagger a_{p-}^\dagger a_{q-} a_{r\mp} \big).
\end{aligned}
$$

Summing over p and q gives

$$
\begin{aligned}
[\hat{V}, \hat{S}_\pm] &= \hat{V} \hat{S}_\pm - \hat{S}_\pm \hat{V} \\
&= \frac{g}{2} \sum_{r} \big(\delta_{\mp+} a_{r\pm}^\dagger a_{r-}^\dagger a_{r-} a_{r+} - \delta_{\mp-} a_{r\pm}^\dagger a_{r+}^\dagger a_{r-} a_{r+} \\
&\qquad + \delta_{\pm-} a_{r+}^\dagger a_{r-}^\dagger a_{r+} a_{r\mp} - \delta_{\pm+} a_{r+}^\dagger a_{r-}^\dagger a_{r-} a_{r\mp} \big).
\end{aligned}
$$

For top

$$
\begin{aligned}
&-a_{r+}^\dagger a_{r+}^\dagger a_{r-} a_{r+} - a_{r+}^\dagger a_{r-}^\dagger a_{r-} a_{r-}. \\
&a_{r-}^\dagger a_{r-}^\dagger a_{r-} a_{r+} + a_{r+}^\dagger a_{r-}^\dagger a_{r+} a_{r+}
\end{aligned}
$$

1   THIS MUST BE FIXED

The commutator $[\hat{H}_0, \hat{S}^2]$

To compute the commutator between $\hat{H}_0$ and $\hat{S}^2$ we express the total spin by the operators $\hat{S}_z$ and $\hat{S}_\pm$, so we get

$$[\hat{H}_0, \hat{S}^2] = [\hat{H}_0, \hat{S}_z^2 + \frac{1}{2}(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+)]$$

$$= [\hat{H}_0, \hat{S}_z^2] + \frac{1}{2}[\hat{H}_0, \hat{S}_+\hat{S}_-] + \frac{1}{2}[\hat{H}_0, \hat{S}_-\hat{S}_+].$$

We now use that fact that for any operators $\hat{A}$, $\hat{B}$ and $\hat{C}$

$$[\hat{A}, \hat{B}\hat{C}] = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}].$$

So we get

$$[\hat{H}_0, \hat{S}_z^2] = [\hat{H}_0, \hat{S}_z]\hat{S}_z + \hat{S}_z[\hat{H}_0, \hat{S}_z] = 0,$$
$$[\hat{H}_0, \hat{S}_+\hat{S}_-] = [\hat{H}_0, \hat{S}_+]\hat{S}_- + \hat{S}_+[\hat{H}_0, \hat{S}_-] = 0,$$
$$[\hat{H}_0, \hat{S}_-\hat{S}_+] = [\hat{H}_0, \hat{S}_-]\hat{S}_+ + \hat{S}_-[\hat{H}_0, \hat{S}_+] = 0.$$

So we see that
$$[\hat{H}_0, \hat{S}^2] = 0.$$

The commutator $[\hat{V}, \hat{S}^2]$

We immediately see that $\hat{V}$ and $\hat{S}^2$ commutes from the same argument as for $\hat{H}_0$.

$$[\hat{V}, \hat{S}^2] = 0.$$

Rewriting the Hamiltonian

We now introduce the pair creation and annihilation operators

$$\hat{P}_p^+ = a_{p+}^\dagger a_{p-}^\dagger \qquad \hat{P}_p^- = a_{p-}a_{p+},$$

which lets us write $\hat{V}$ as
$$\hat{V} = -\frac{1}{2}g\sum_{pq} \hat{P}_p^+ \hat{P}_q^-.$$

If we also set $\xi = 1$, we can write the full Hamiltonian as

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_{p\sigma}(p-1)a_{p\sigma}^\dagger a_{p\sigma} - \frac{1}{2}g\sum_{pq}\hat{P}_p^+\hat{P}_q^-.$$

The commutator $[\hat{H}, \hat{P}_p^+\hat{P}_q^-]$

Summary of commutators

We have shown that $\hat{H}_0$ and $\hat{V}$ both commute with $\hat{S}_z$, $\hat{S}_\pm$ and $\hat{S}^2$.

Exercise 2)

We now look at a system with four particles. We limit our system to have no broken pairs and always have a total spin of $S = 0$. We also limit our system to only inhabit the four lowest levels $p = 1, 2, 3, 4$. This gives rise to six different Slater determinants

$$|\Phi^{12}\rangle = \hat{P}_1^+ \hat{P}_2^+ |0\rangle, \qquad |\Phi^{13}\rangle = \hat{P}_1^+ \hat{P}_3^+ |0\rangle, \qquad |\Phi^{14}\rangle = \hat{P}_1^+ \hat{P}_4^+ |0\rangle,$$
$$|\Phi^{23}\rangle = \hat{P}_2^+ \hat{P}_3^+ |0\rangle, \qquad |\Phi^{24}\rangle = \hat{P}_2^+ \hat{P}_4^+ |0\rangle, \qquad |\Phi^{34}\rangle = \hat{P}_3^+ \hat{P}_4^+ |0\rangle.$$

These Slater determinants are illustrated in figure 1.
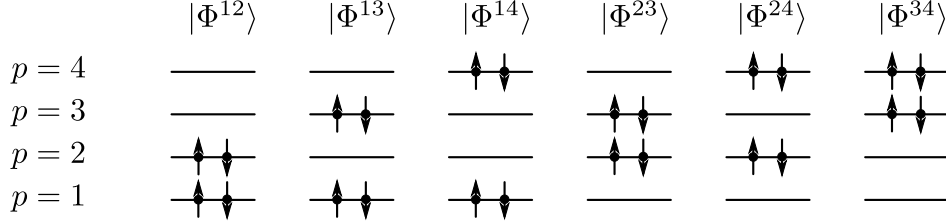
Figure 1. Sketch of the six possible Slater determinants.

These six Slater determinants are orthonormal and span a six-dimensional Hilbert space. We want to compute the matrix representation of the Hamiltonian in this space, which is given by

$$H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle,$$

where $\{\Phi_i\}_{i=1}^6$ is the set of the six Slater determinants. To calculate the different matrix elements, it's easiest to split up the Hamiltonian, so we have

$$H_{ij} = \langle \Phi_i | \hat{H}_0 | \Phi_j \rangle + \langle \Phi_i | \hat{V} | \Phi_j \rangle.$$

The one-body operator is

$$\sum_{p\sigma} (p-1) a_{p\sigma}^\dagger a_{p\sigma},$$

so we see that the for the off-diagonal terms, the one-body contribution vanishes. For the diagonal terms we find

$$\langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 2, \qquad \langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 4, \qquad \langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 6,$$
$$\langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 6, \qquad \langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 8, \qquad \langle \Phi^{12} | \hat{H}_0 | \Phi^{12} \rangle = 10.$$

For the two-body operator we have

$$\langle \Phi^{ij} | \hat{V} | \Phi^{kl} \rangle = -\frac{g}{2} \sum_{pq} \langle 0 | \hat{P}_i \hat{P}_j \hat{P}_p^+ \hat{P}_q \hat{P}_k^+ \hat{P}_l^+ | 0 \rangle.$$

There can be two, one or no non-coincidences between the Slater determinants. If there are two non-coincidences, we see that the matrix element vanishes as we can only remove one non-coincidence. If there is one non-coincidence we have

$$\langle \Phi^{ij} | \hat{V} | \Phi^{ik} \rangle = -\frac{g}{2} \sum_{pq} \langle 0 | \hat{P}_i \hat{P}_j \hat{P}_p^+ \hat{P}_q \hat{P}_i^+ \hat{P}_k^+ | 0 \rangle.$$

When we sum over p and q, the only term that survives is the term were $p = j$ and $q = k$, all other terms vanish due to the orthogonality of the the Slater determinants, so we

If there are no non-coincidences, we have

$$\langle \Phi^{ij}|\hat{V}|\Phi^{ij}\rangle = -\frac{g}{2}\sum_{pq}\langle 0|\hat{P}_i\hat{P}_j\hat{P}_p^+\hat{P}_q\hat{P}_i^+\hat{P}_j^+|0\rangle$$

The only terms that survive in the sums are now the terms were $p = q = i$ or $p = q = j$, so we get two terms contributing to the final result.

We can then set up the Hamiltonian matrix

$$\hat{H} = \begin{pmatrix} 2-g & -g/2 & -g/2 & -g/2 & -g/2 & 0 \\ -g/2 & 4-g & -g/2 & -g/2 & 0 & -g/2 \\ -g/2 & -g/2 & 6-g & 0 & -g/2 & -g/2 \\ -g/2 & -g/2 & 0 & 6-g & -g/2 & -g/2 \\ -g/2 & 0 & -g/2 & -g/2 & 8-g & -g/2 \\ 0 & -g/2 & -g/2 & -g/2 & -g/2 & 10-g \end{pmatrix}$$

Numerically, we find the eigenvalues and eigenvectors

$$\lambda = \begin{pmatrix} 0.780 \\ 9.364 \\ 7.065 \\ 5.000 \\ 2.791 \\ 5.000 \end{pmatrix}, \quad V = \begin{pmatrix} 0.972 & -0.041 & -0.104 & -0.154 & -0.136 & 0.004 \\ -0.185 & -0.101 & -0.014 & -0.309 & -0.927 & 0.008 \\ -0.089 & -0.154 & -0.170 & -0.617 & 0.242 & -0.691 \\ -0.089 & -0.154 & -0.170 & -0.617 & 0.242 & 0.723 \\ -0.066 & -0.271 & -0.908 & 0.309 & -0.046 & -0.008 \\ 0.026 & -0.931 & 0.326 & 0.154 & 0.039 & -0.004 \end{pmatrix}.$$
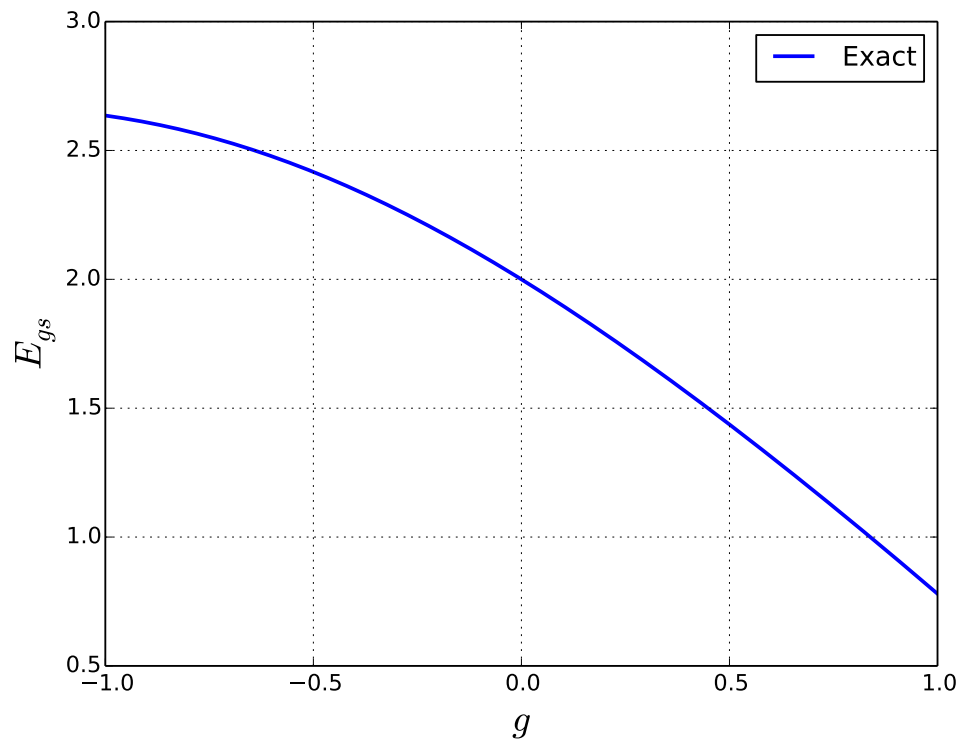
Figure 2. Ground state energy as a function of the interaction-parameter g.

Exercise 3)

We now limit our system to at most two-particle-two-hole excitations. This means we discard $|\Phi^{34}\rangle$, and only look at a five-dimensional system.

The Hamiltonian matrix is then the five-by-five matrix

$$\hat{H} = \begin{pmatrix} 2-g & -g/2 & -g/2 & -g/2 & -g/2 \\ -g/2 & 4-g & -g/2 & -g/2 & 0 \\ -g/2 & -g/2 & 6-g & 0 & -g/2 \\ -g/2 & -g/2 & 0 & 6-g & -g/2 \\ -g/2 & 0 & -g/2 & -g/2 & 8-g \end{pmatrix}$$

Exercise 4)

We now turn to Hartree-Fock theory, we will define our model space to consist of the single-particle levels $p = 1, 2$ and the excluded space is then $p = 3, 4$. This means we also define our reference state to be

$$|\Phi_0\rangle = \hat{P}_1^+ \hat{P}_2^+ |0\rangle.$$

The projection operator $\hat{P}$ projects onto the model space, which is spanned by the reference function, so $\hat{P} = |\Phi_0\rangle\langle\Phi_0|$.

Partitioning the Hamiltonian

If we limit ourselves to at most two-body interactions, the Hamiltonian can be generally written as a sum of one-body and two-body operators, which in second quantization looks like

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_\mu \hat{h}_\mu + \sum_{\mu\nu} \hat{v}_{\mu\nu}.$$

For our system we have a single one-body and a single two-body interaction, labeling them $\hat{h}_0$ and $\hat{v}$, we get

$$\hat{H} = \sum_{\alpha\beta} \langle\alpha|\hat{h}_0|\beta\rangle \alpha^\dagger \beta + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta||\gamma\delta\rangle \alpha^\dagger\beta^\dagger\delta\gamma,$$

where we use Shavitt and Bartlet's shorthand of $\langle\alpha\beta||\gamma\delta\rangle = \langle\alpha\beta|\hat{v}|\gamma\delta\rangle_{\text{AS}}$.

Using Wick's theorem, we can write these out as

$$\hat{H}_1 = \sum_{pq} \langle p|\hat{h}_0|q\rangle \{\hat{p}^\dagger\hat{q}\} + \sum_i \langle i|\hat{h}_0|i\rangle,$$

$$\hat{H}_2 = \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \sum_{pqi} \langle pi||qi\rangle \{\hat{p}^\dagger\hat{q}\} + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle.$$

We now define the *reference energy* as

$$E_{\text{ref}} = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle.$$

Which enables us to split the Hamiltonian into its normal-ordered part and the reference energy

$$\hat{H} = \hat{H}_{\text{N}} + E_{\text{ref}}.$$

The normal-ordered Hamiltonian is then

$$\hat{H}_{\text{N}} = \sum_{pq} \langle p|\hat{h}_0|q\rangle \{\hat{p}^\dagger\hat{q}\} + \sum_{pqi} \langle pi||qi\rangle \{\hat{p}^\dagger\hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}.$$

We now relabel the first two terms into the normal-ordered *Fock-operator*, giving us

$$\hat{H}_{\text{N}} = \hat{F} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}.$$

We can now think of the normal-ordered Hamiltonian as the sum of a one-body part and the perturbation

$$\hat{W}_{\text{N}} = \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\},$$

we will get back to this when we turn to many-body perturbation theory.

For now, we will look closer at the normal-ordered Fock-operator

$$\hat{F}_N = \sum_{pq} \langle p|\hat{h}_0|q\rangle \{\hat{p}^\dagger \hat{q}\} + \sum_{pqi} \langle pi||qi\rangle \{\hat{p}^\dagger \hat{q}\} = \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\},$$

where

$$f_{pq} = \langle p|\hat{h}_0|q\rangle + \sum_{pqi} \langle pi||qi\rangle \{\hat{p}^\dagger \hat{q}\} = h_{pq} + u_{pq}.$$

We see that the exact form of the Fock-matrix is then the result of the one-body and two-body operators $\hat{h}_0$ and $\hat{v}$ and also of our choice of single-particle basis.

The form of the Fock-matrix is quite important for our further discussion of how to solve the problem, and so we will label three different general cases.

1. First we have the possibility of the Fock-matrix being purely diagonal

$$f_{pq} = \epsilon_p \delta_{pq},$$

   this case is known as the *cannonical Hartree-Fock* case.

2. Next, we have the case where the Fock-matrix is not entirely diagonal, but it is *block-diagonal*, meaning the blocks of the Fock-matrix corresponding to the matrix elements between hole and particle states vanish. So we have

$$f_{ai} = 0,$$

   this is the *non-cannonical* Hartree-Fock case. Note that some people do not distinguish between the cannonical and non-cannonical HF cases.

3. All cases not covered by the two HF cases are collectively reffered to as *general* cases.

As the normal-ordered Fock-operator can be non-diagonal, it is often conveniant to split it into its diagonal and off-diagonal contributions

$$\hat{F}_N = \sum_{p} f_{pp} \{\hat{p}^\dagger \hat{p}\} + \sum_{p \neq q} f_{pq} \{\hat{p}^\dagger \hat{q}\} = \hat{F}_N^D + \hat{F}_N^O.$$

In the cases where $\hat{F}_N^O \neq 0$, it is common to include this part of the Fock-operator in the perturbation.

The total normal-product Hamiltonian is then

$$\hat{H}_N = \hat{F}_N + \hat{W} = \hat{F}_N^d + \hat{F}_N^o + \hat{W} = \hat{F}_N^d + \text{(perturbation)}.$$

In our basis, we have

$$f_{pq} = \langle p|\hat{h}_0|q\rangle \{\hat{p}^\dagger \hat{q}\} + \sum_{i} \langle pi||qi\rangle \{\hat{p}^\dagger \hat{q}\}.$$

Here the state indices run over both the quantum numberd p and σ. As we have no $1p1h$-states, only $2p2h$-states, there will either be zero or two noncoincidences between states. This means that $\{\hat{p}^\dagger \hat{q}\}$

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_{p\sigma}(p-1)a_{p\sigma}^\dagger a_{p\sigma} - \frac{1}{2}g\sum_{pq}a_{p+}^\dagger a_{p-}^\dagger a_{q-}a_{q+}.$$

Canonical and non-canonical Hartree-Fock

For canonical Hartree-Fock, we now that the Fock-operator is diagonal, meaning

$$f_{pq} = \epsilon_p \delta_{pq}, \qquad \epsilon_p = h_{pp} + \sum_i \langle pi||pi\rangle.$$

For the non-canonical Hartree-Fock, the Fock-operator is a block-diagonal matrix, this means that f_{ai} is zero, but f_{ab} and f_{ij} are generally not zero. For the completely general case, there is no guarantee that any element of the Fock matrix is zero.

$$\hat{H} = \sum_{pq} p^\dagger q + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle p^\dagger q^\dagger sr.$$

$$\hat{H}_0 = \sum_{pq}\langle p|\hat{h}_0|q\rangle\{\hat{p}^\dagger\hat{q}\} + \sum_i\langle i|\hat{h}_0|i\rangle,$$

$$\hat{H}_1 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle_{\text{AS}}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \sum_{pqi}\langle pi|\hat{v}|qi\rangle_{\text{AS}}\{\hat{p}^\dagger\hat{q}\} + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle_{\text{AS}}.$$

We can then see that we have the Fock-operator

$$\hat{F} = \sum_{pq}\langle p|\hat{h}_0|q\rangle\{\hat{p}^\dagger\hat{q}\} + \sum_{pqi}\langle p||q\rangle\{\hat{p}^\dagger\hat{q}\}.$$

So that the matrix elements of the Fock-matrix are given by

$$f_{pq} = h_{pq} + \sum_i\langle pi||qi\rangle.$$

We then have

$$\hat{H} = \hat{F} + \hat{E}_{ref} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle,$$

where

$$E_{ref} = \sum_i\langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle.$$

So we have

$$\hat{H}_{\text{N}} = \hat{F} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle.$$

If we are looking at canonical HF

$$f_{pq} = \epsilon_p \delta_{pq}.$$

If we are looking at non-canonical HF

Exercise 5)

Diagram 3 vanishes due to the nature of the interaction.

Diagram 2 is only in non-can, diagram 6, 7, 6, 10, 11, 12, 13, 14, 15 and 16 all vanish.

We define the reference vacuum, which is our ansatz for the ground state $|\Phi_0\rangle$. We can define 1p-1h and 2p-2h excitations as $\hat{T}_1|\Phi_0\rangle$ and $\hat{T}_2|\Phi_0\rangle$.

We usually use the non-interacting part of the Hamiltonian as our single-particle wave functions.

We can then expand our exact ground state as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\phi_i^a\rangle + \sum_{abij} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \ldots = (C_0 + \hat{C})|\Phi_0\rangle.$$

Where we have introduced the correlation operators

$$\hat{C} = \sum_{ai} C_i^a \hat{a}_a^\dagger \hat{a}_i + \sum_{abij} C_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$$

We now set $C_0 = 1$, giving

$$|\Psi_0\rangle = (1 + \hat{C})|\Phi_0\rangle.$$

$$|\Psi_0\rangle = \sum_{PH} C_H^P \Phi_H^P.$$

For all PH sets we get

$$\sum_{P'H'} \langle \Phi_H^P|\hat{H} - E|\Phi_{H'}^{P'}\rangle = 0.$$

In Perturbation theory we assume that the exact ground state wave function is dominated by $|\Phi_0\rangle$ and can be written in intermediate normalization as

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m|\Phi_m\rangle.$$

From the Schrödinger equation, we have

$$\langle \Phi_0|\hat{H}|\Psi_0\rangle = E,$$

And

$$\langle \Psi_0|\hat{H}_0|\Phi_0\rangle = W_0,$$

so we can define

$$\Delta E = E - W_0 = \langle \Phi_0|\hat{H}_I|\Psi_0\rangle.$$

This quantity is called the correlation energy.

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0|,$$

$$\hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|.$$

$$|\Psi_0\rangle = (\hat{P} + \hat{Q})|\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle.$$

$$\chi_n = |\Psi_n\rangle - |\Phi_n\rangle.$$

$$\langle \Phi_n|\Phi_n\rangle = 1, \quad \langle \Psi_n|\Phi_n\rangle = 1, \quad \langle \chi_n|\Phi_n\rangle = 0, \quad \langle \Psi_n|\Psi_n\rangle = 1 + \langle \chi_n|\chi_n\rangle.$$

Idempotenence

$$\hat{P}^2 = \hat{P}, \quad \hat{Q}^2 = \hat{Q}$$

$$\hat{P}\hat{Q} = 0.$$

The operator $\hat{P}$ projects the component of Ψ that is parallel to Φ_0, which can be seen from

$$\hat{P}\Psi = \sum_{a_i} |\Phi_0\rangle\langle\Phi_0||\Phi_i\rangle = a_0|\Phi_0\rangle.$$

While $\hat{Q}$ annihilates the Φ_0 component, leaving everything else intact. This also means that

$$\Psi = (\hat{P} + \hat{Q})\Psi.$$

Exercise 7)

Linked and unlinked diagrams

A diagram is called unlinked if and only if it has a disconnected part that is closed, meaning it has no open lines.

Goldstones linked-diagram theorem states that all unliked diagrams will cancel agains the renormalization terms in RSPT, meaning we can express the energy and wave function in each order as a sum of linked diagrams only [1]. This means we have

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[1] See Shavitt and Bartlet section 5.8.

In general, we have

$$\left(E^{(0)} - \hat{H}\right)\Psi^{(m)} = (E^{(1)} - \hat{V})\Psi^{(m-1)} - \sum_{l=0}^{m-1} E^{m-l}\Psi^{(l)}.$$

We can apply $\langle\Phi|$ to the equation and find

$$E^{(m)} = \langle\Phi|\hat{V}|\Psi^{(m-1)}\rangle.$$

As ξ is only a scalar that is multiplied with H_0, and we already the scaling g, we can se the parameter ξ equal to 1, without a loss of generality.

Decompose the solution into

$$\Psi = (\hat{P} + \hat{Q})\Psi = \hat{P}\Psi + \hat{Q}\Psi = \Phi + \chi.$$

$$\Psi = \sum_{m=0}^{\infty} \left[\hat{R}_0(\hat{V} - \hat{E})\right]^m \Phi,$$

$$\Delta E = \sum_{m=0}^{\infty} \langle\Phi|\hat{V}\left[\hat{R}_0(\hat{V} - \hat{E})\right]^m|\Phi\rangle$$

Cannonical HF

$$f_{pq} = \epsilon_p \delta_{pq}$$

$$\epsilon_p = h_{pp} + \sum_i \langle pi||pi\rangle.$$

Non-cannonical HF

$$f_{ia} = 0.$$

Fock-operator

$$\hat{F} = \sum_{pq} f_{pq}\hat{p}^\dagger\hat{q}.$$

$$\hat{U} = \sum_{pq} u_{pq}\hat{p}^\dagger\hat{q}.$$

$$\hat{F} = \hat{H}_0 + \hat{U} = \sum_{pq}(h_{pq} + u_{pq})\hat{p}^\dagger\hat{q}.$$

$$\hat{u} = \sum_i (\hat{J}_i - \hat{K}_i).$$

The normal-product Schrodinger equation is

$$\hat{H}_{\mathrm{N}}\Psi = \Delta E\Psi,$$

where ΔE is the correlation energy in the Hartree-Fock case, the normal-product Hamiltonian is

$$\hat{H}_{\mathrm{N}} = \hat{F}_{\mathrm{N}} + \hat{W} = \hat{F}_{\mathrm{N}}^d + \hat{F}^o + \hat{W} = \hat{F}^d + \hat{V}_{\mathrm{N}}.$$