## (A.)

1. Show that the states $|S_{\alpha,\beta}\rangle$ $\alpha,\beta \in \{Cu, O\}$ are singlets. To show that $(S_\alpha^- + S_\beta^-)|S_{\alpha,\beta}\rangle = 0$ and $(S_\alpha^z + S_\beta^z)|S_{\alpha,\beta}\rangle = 0$, we use the fermionic anticommutation relations and the fact that acting on the vacuum $|0\rangle$ with the annhilation operators gives zero.

$$\begin{aligned}(S^-_{\mathrm{Cu}_1} + S^-_{\mathrm{Cu}_2})|S_{\mathrm{Cu,Cu}}\rangle &= (d^\dagger_{1,\downarrow}d_{1,\uparrow} + d^\dagger_{2,\downarrow}d_{2,\uparrow})\tfrac{1}{\sqrt{2}}(d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} - d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow})|0\rangle \\ &= \tfrac{1}{\sqrt{2}}(d^\dagger_{1,\downarrow}d^\dagger_{2,\downarrow} + d^\dagger_{2,\downarrow}d^\dagger_{1,\downarrow})|0\rangle \\ &= 0\end{aligned} \tag{1}$$

and

$$\begin{aligned}(S^z_{\mathrm{Cu}_1} + S^z_{\mathrm{Cu}_2})|S_{\alpha,\beta}\rangle &= \tfrac{1}{2}\left((n_{d_{1,\uparrow}} - n_{d_{1,\downarrow}}) + (n_{d_{2,\uparrow}} - n_{d_{2,\downarrow}})\right)\tfrac{1}{\sqrt{2}}(d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} - d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow})|0\rangle \\ &= \tfrac{1}{2\sqrt{2}}\left(1\cdot d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} + 1\cdot d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow} - 1\cdot d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow} - 1\cdot d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow}\right)|0\rangle \\ &= 0\end{aligned} \tag{2}$$

In the same way it can be shown that these two equalities are valid for the other three ways of constructing singlet states.

2. Show that the states $|T^\gamma_{\alpha,\beta}\rangle$ $\alpha,\beta \in \{Cu, O\}$, $\gamma \in \{1, 0, -1\}$ are triplets. We study the case of triplets built with one electron on each copper atom:

$$\begin{aligned}&\tfrac{1}{2}\left((n_{d_{1,\uparrow}} - n_{d_{1,\downarrow}}) + (n_{d_{2,\uparrow}} - n_{d_{2,\downarrow}})\right)d^\dagger_{1,\uparrow}d^\dagger_{2,\uparrow}|0\rangle = \tfrac{1}{2}2d^\dagger_{1,\uparrow}d^\dagger_{2,\uparrow}|0\rangle \\ &\tfrac{1}{2}\left((n_{d_{1,\uparrow}} - n_{d_{1,\downarrow}}) + (n_{d_{2,\uparrow}} - n_{d_{2,\downarrow}})\right)d^\dagger_{1,\downarrow}d^\dagger_{2,\downarrow}|0\rangle = \tfrac{1}{2}(-2)d^\dagger_{1,\downarrow}d^\dagger_{2,\downarrow}|0\rangle \\ &\tfrac{1}{2}\left((n_{d_{1,\uparrow}} - n_{d_{1,\downarrow}}) + (n_{d_{2,\uparrow}} - n_{d_{2,\downarrow}})\right)\tfrac{1}{\sqrt{2}}(d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} + d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow})|0\rangle = \\ &\quad = \tfrac{1}{2\sqrt{2}}\left(1\cdot d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} - 1\cdot d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow} + 1\cdot d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow} - 1\cdot d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow}\right)|0\rangle \\ &\quad = 0\end{aligned} \tag{3}$$

It remains to show that the state $|T^0_{\mathrm{Cu,Cu}}\rangle$ is indeed orthogonal to the singlet $|S_{\mathrm{Cu,Cu}}\rangle$.

$$\begin{aligned}\langle S_{\mathrm{Cu,Cu}}|T^0_{\mathrm{Cu,Cu}}\rangle &= \tfrac{1}{2}\langle 0|(d_{2,\downarrow}d_{1,\uparrow} - d_{2,\uparrow}d_{1,\downarrow})(d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} + d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow})|0\rangle \\ &= \tfrac{1}{2}\langle 0|(d_{2,\downarrow}d_{1,\uparrow}d^\dagger_{1,\uparrow}d^\dagger_{2,\downarrow} - d_{2,\uparrow}d_{1,\downarrow}d^\dagger_{1,\downarrow}d^\dagger_{2,\uparrow})|0\rangle \\ &= \tfrac{1}{2}\langle 0|(d_{2,\downarrow}d^\dagger_{2,\downarrow} - d_{2,\uparrow}d^\dagger_{2,\uparrow})|0\rangle \\ &= \tfrac{1}{2}\langle 0|(1 - d^\dagger_{2,\downarrow}d_{2,\downarrow}) - (1 - d^\dagger_{2,\uparrow}d_{2,\uparrow})|0\rangle \\ &= 0\end{aligned} \tag{4}$$

3. The elements of the $\mathcal{B}$ basis are eigenstates of $\mathcal{H}_\Delta$ et $\mathcal{H}_H$.

- The Hamiltonian $\mathcal{H}_\Delta$ counts the number of electrons that are on $p$ orbitals. It costs the system an energy $\Delta$ to have an electron on a $p$ orbital, and an energy $2\Delta$ to have an electron on each $p$ orbitals.
- By switching the operators in $\mathcal{H}_H$ we get an operator of the form

$$\mathcal{H}_H = \sum_{\sigma,\sigma'} O_{\sigma,\sigma'} p_{x,\sigma} p_{y\sigma'} \tag{5}$$

  where the form of the operators $O_{\sigma,\sigma'}$ is not important. It follows that the effect of $\mathcal{H}_H$ applied to a state that does not have any electrons on p orbitals is equal to zero. Moreover $\mathcal{H}_H$ corresponds to a ferromagnetic Heisenberg interaction (see previous series) between the electrons that are on the orbital $p_x$ and $p_y$. The triplet states $|T^1_{\mathrm{O,O}}\rangle, |T^0_{\mathrm{O,O}}\rangle$ and $|T^{-1}_{\mathrm{O,O}}\rangle$ are eigenstates of $\mathcal{H}_H$ energy $-J_H/4$ and the singlet $|S_{\mathrm{O,O}}\rangle$ is the state of energy $3J_H/4$.

It follows that:

$$\left\{|T^1_{Cu,Cu}\rangle, |T^0_{Cu,Cu}\rangle, |T^{-1}_{Cu,Cu}\rangle, |S_{Cu,Cu}\rangle\right\} \tag{6}$$

is the ground subspace of $\mathcal{H}_0$ of energy $E_0 = 0$.

$$\left\{|T^1_{Cu,O}\rangle, |T^0_{Cu,O}\rangle, |T^{-1}_{Cu,O}\rangle, |S_{Cu,O}\rangle, |T^1_{O,CU}\rangle, |T^0_{O,Cu}\rangle, |T^{-1}_{O,Cu}\rangle, |S_{O,Cu}\rangle\right\} \tag{7}$$

is the eigen subspace of $\mathcal{H}_0$ of energy $E = \Delta$

$$\left\{|T^1_{O,O}\rangle, |T^0_{O,O}\rangle, |T^{-1}_{O,O}\rangle\right\} \tag{8}$$

is the eigen subspace of $\mathcal{H}_0$ of energy $E = 2\Delta - J_H/4$ (as we are in the case $J_H \ll \Delta$, $2\Delta - J_H/4 > 0$).
Finally the state

$$|S_{O,O}\rangle \tag{9}$$

is an eigen state of energy $E = 2\Delta + 3J_H/4$.

4. We calculate

$$\begin{aligned}
\mathcal{H}_t|T^1_{Cu,Cu}\rangle &= \mathcal{H}_t d^\dagger_{1,\uparrow} d^\dagger_{2,\uparrow}|0\rangle & \mathcal{H}_t|T^{-1}_{Cu,Cu}\rangle &= \mathcal{H}_t d^\dagger_{1,\downarrow} d^\dagger_{2,\downarrow}|0\rangle \\
&= -t(p^\dagger_{x,\uparrow} d_{1,\uparrow} + p^\dagger_{y,\uparrow} d_{2,\uparrow}) d^\dagger_{1,\uparrow} d^\dagger_{2,\uparrow}|0\rangle & &= -t(p^\dagger_{x,\downarrow} d_{1,\downarrow} + p^\dagger_{y,\downarrow} d_{2,\downarrow}) d^\dagger_{1,\downarrow} d^\dagger_{2,\downarrow}|0\rangle \\
&= -t\left(|T^1_{O,Cu}\rangle + |T^1_{Cu,O}\rangle\right) & &= -t\left(|T^{-1}_{O,Cu}\rangle + |T^{-1}_{Cu,O}\rangle\right)
\end{aligned} \tag{10}$$

$$\begin{aligned}
\mathcal{H}_t|T^0_{Cu,Cu}\rangle &= \mathcal{H}_t \tfrac{1}{\sqrt{2}}(d^\dagger_{1,\uparrow} d^\dagger_{2,\downarrow} + d^\dagger_{1,\downarrow} d^\dagger_{2,\uparrow})|0\rangle \\
&= \tfrac{-t}{\sqrt{2}}\left[(p^\dagger_{x,\uparrow} d_{1,\uparrow} + p^\dagger_{y,\downarrow} d_{2,\downarrow}) d^\dagger_{1,\uparrow} d^\dagger_{2,\downarrow} + (p^\dagger_{x,\downarrow} d_{1,\downarrow} + p^\dagger_{y,\uparrow} d_{2,\uparrow}) d^\dagger_{1,\downarrow} d^\dagger_{2,\uparrow}\right]|0\rangle \\
&= -t\left(|T^0_{O,Cu}\rangle + |T^0_{Cu,O}\rangle\right)
\end{aligned} \tag{11}$$

$$\begin{aligned}
\mathcal{H}_t|T^0_{Cu,Cu}\rangle &= \mathcal{H}_t \tfrac{1}{\sqrt{2}}(d^\dagger_{1,\uparrow} d^\dagger_{2,\downarrow} - d^\dagger_{1,\downarrow} d^\dagger_{2,\uparrow})|0\rangle \\
&= \tfrac{-t}{\sqrt{2}}\left[(p^\dagger_{x,\uparrow} d_{1,\uparrow} + p^\dagger_{y,\downarrow} d_{2,\downarrow}) d^\dagger_{1,\uparrow} d^\dagger_{2,\downarrow} - (p^\dagger_{x,\downarrow} d_{1,\downarrow} + p^\dagger_{y,\uparrow} d_{2,\uparrow}) d^\dagger_{1,\downarrow} d^\dagger_{2,\uparrow}\right]|0\rangle \\
&= -t\left(|S^0_{O,Cu}\rangle + |S^0_{Cu,O}\rangle\right)
\end{aligned} \tag{12}$$

Likewise, it is shown that these relations are satisfied by the other elements of the basis.

5. In the previous question we have shown that $\mathcal{H}_t$ applied to any state of the ground subspace $\left\{|T^1_{Cu,Cu}\rangle, |T^0_{Cu,Cu}\rangle, |T^{-1}_{Cu,Cu}\rangle, |S_{Cu,Cu}\rangle\right\}$ gives an orthogonal state to the ground subspace. $P_0$ being the projector on the ground subspace, we have $P_0\mathcal{H}_tP_0 = 0$.

   The different terms of $\mathcal{H}^{(4)}_{\text{eff}}$ are written with the projector $P_0$ left and right, separated by a chain of operators. If in the operator string $\mathcal{H}_t$ appears three times, it amounts to considering a process that has three electron hops. According to the previous question we deduce that starting from any state of the ground subspace it is impossible to return to a state of the ground subspace by applying $\mathcal{H}_t$ three times. We deduce that the terms of order 3 in $\mathcal{H}_t$ dans $\mathcal{H}^{(4)}_{\text{eff}}$ are null.

6. We apply $\mathcal{H}^{(2)}_{\text{eff}} = P_0VSVP_0$ to the state of the ground subspace

$$\begin{aligned}
P_0VSVP_0|T_{\text{Cu,Cu}}\rangle &= P_0VS(-t)\left(|T^1_{O,Cu}\rangle + |T^1_{Cu,O}\rangle\right)\\
&= P_0V(-t)\tfrac{1}{-\Delta}\left(|T^1_{O,Cu}\rangle + |T^1_{Cu,O}\rangle\right)\\
&= P_0(-t)^2\tfrac{2}{-\Delta}\left(|T^1_{O,O}\rangle + |T^1_{Cu,Cu}\rangle\right)\\
&= -\tfrac{2t^2}{\Delta}|T^1_{Cu,Cu}\rangle
\end{aligned} \tag{13}$$

   If we repeat the computation for the other elements of the ground subspace we obtain that $P_0VSVP_0$ is diagonal:

$$-\frac{2t^2}{\Delta}\begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{14}$$

   The perturbation does not lift the degeneracy of the ground subspace at the 2nd order. It will only be lifted at 4th order in $\mathcal{H}_t$.

7. We try to calculate the effect of $P_0VS^2VP_0VSVP_0$ on the ground subspace:

$$\begin{aligned}
P_0VS^2VP_0VSVP_0|T^1_{\text{Cu,Cu}}\rangle &= (-t)P_0VS^2VP_0VS(|T^1_{\text{O,Cu}}\rangle + |T^1_{\text{Cu,O}}\rangle)\\
&= \tfrac{-t}{-\Delta}P_0VS^2VP_0V(|T^1_{\text{O,Cu}}\rangle + |T^1_{\text{Cu,O}}\rangle)\\
&= \tfrac{2(-t)^2}{-\Delta}P_0VS^2V|T^1_{\text{Cu,Cu}}\rangle\\
&= \tfrac{2(-t)^3}{-\Delta}P_0VS^2(|T^1_{\text{O,Cu}}\rangle + |T^1_{\text{Cu,O}}\rangle)\\
&= \tfrac{2(-t)^3}{(-\Delta)^3}P_0V(|T^1_{\text{O,Cu}}\rangle + |T^1_{\text{Cu,O}}\rangle)\\
&= -\tfrac{4t^4}{\Delta^3}|T^1_{\text{Cu,Cu}}\rangle
\end{aligned} \tag{15}$$

   If we look for the other states of the ground subspace we get:

$$P_0VS^2VP_0VSVP_0 = -\frac{4t^4}{\Delta^3}\begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{16}$$

   The result is the same for $P_0VSVP_0VS^2VP_0$.

8. The effect of $P_0VSVSVSVP_0$ on the ground subspace is as follows:

$$\begin{array}{rcl} P_0VSVSVSVP_0|T^1_{\mathrm{Cu,Cu}}\rangle & = & -\frac{4t^4}{\Delta^2(2\Delta-\frac{J_H}{4})}|T^1_{\mathrm{Cu,Cu}}\rangle \\ P_0VSVSVSVP_0|T^{-1}_{\mathrm{Cu,Cu}}\rangle & = & -\frac{4t^4}{\Delta^2(2\Delta-\frac{J_H}{4})}|T^{-1}_{\mathrm{Cu,Cu}}\rangle \\ P_0VSVSVSVP_0|T^0_{\mathrm{Cu,Cu}}\rangle & = & -\frac{4t^4}{\Delta^2(2\Delta-\frac{J_H}{4})}|T^0_{\mathrm{Cu,Cu}}\rangle \\ P_0VSVSVSVP_0|S_{\mathrm{Cu,Cu}}\rangle & = & -\frac{4t^4}{\Delta^2(2\Delta+\frac{3J_H}{4})}|S_{\mathrm{Cu,Cu}}\rangle \end{array} \tag{17}$$

9. In the basis $\left\{|T^1_{\mathrm{Cu,Cu}}\rangle, |T^{-1}_{\mathrm{Cu,Cu}}\rangle, |T^0_{\mathrm{Cu,Cu}}\rangle, |S_{\mathrm{Cu,Cu}}\rangle\right\}$, $\mathcal{H}^{(4)}_{\mathrm{eff}}$ reads:

$$\mathcal{H}^{(4)}_{\mathrm{eff}} = \begin{pmatrix} a & 0 & 0 & 0 \\ 0 & a & 0 & 0 \\ 0 & 0 & a & 0 \\ 0 & 0 & 0 & b \end{pmatrix} \tag{18}$$

where $a = -\frac{2t^2}{\Delta} + \frac{4t^4}{\Delta^2}\left(\frac{1}{\Delta} - \frac{1}{2\Delta-\frac{J_H}{4}}\right)$ and $b = -\frac{2t^2}{\Delta} + \frac{4t^4}{\Delta^2}\left(\frac{1}{\Delta} - \frac{1}{2\Delta+\frac{3J_H}{4}}\right)$. We see that the favored spin configurations are $\left\{|T^1_{\mathrm{Cu,Cu}}\rangle, |T^{-1}_{\mathrm{Cu,Cu}}\rangle, |T^0_{\mathrm{Cu,Cu}}\rangle\right\}$. The exchange mechanism described in this series leads to an effective coupling that is ferromagnetic between the two copper atoms.

## (B.) Holstein-Primakoff bosons:

We consider the Holstein-Primakoff transformation

$$\begin{cases} S_+ = \left(\sqrt{2s-\hat{n}}\right) b \\ S_- = b^\dagger \left(\sqrt{2s-\hat{n}}\right) \\ S_z = s - \hat{n} \end{cases} \tag{19}$$

with $\hat{n} = b^\dagger b$.

1. We have

$$\begin{array}{rcl} [S_+, S_-] & = & S_+S_- - S_-S_+ \\ & = & \left(\sqrt{2s-\hat{n}}\right) \underbrace{bb^\dagger}_{1+b^\dagger b} \left(\sqrt{2s-\hat{n}}\right) - b^\dagger \left(\sqrt{2s-\hat{n}}\right)\left(\sqrt{2s-\hat{n}}\right) b \\ & = & (2s-\hat{n}) + \left(\sqrt{2s-\hat{n}}\right)\hat{n}\left(\sqrt{2s-\hat{n}}\right) - b^\dagger(2s-\hat{n})\, b \end{array}$$

but $[b^\dagger b, b^\dagger b] = 0 \Rightarrow [b^\dagger b, \sqrt{2s - b^\dagger b}] = 0$ et $\hat{n}b = b^\dagger bb = (bb^\dagger - 1)b = b\hat{n} - b$

$$\begin{array}{rcl} \Rightarrow [S_+, S_-] & = & (2s-\hat{n}) + \hat{n}(2s-\hat{n}) - \hat{n}(2s-\hat{n}+1) \\ & = & 2s - 2\hat{n} \\ & = & 2S_z \end{array}$$

For $[S_z, S_\pm]$, we have

$$\begin{array}{rcl} [S_z, S_+] & = & [s-\hat{n}, \left(\sqrt{2s-\hat{n}}\right) b] \\ & = & -\left(\sqrt{2s-\hat{n}}\right)\underbrace{[\hat{n}, b]}_{=-b} - \underbrace{[\hat{n}, \left(\sqrt{2s-\hat{n}}\right)]}_{=0} b \\ & = & \left(\sqrt{2s-\hat{n}}\right) b \\ & = & S_+ \end{array}$$

and $[S_z, S_-] = -[S_z, S_+]^\dagger = -S_-$.

2. Using

$$\begin{aligned} b^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\ b|n\rangle &= \sqrt{n}|n-1\rangle \\ \hat{n}|n\rangle &= n|n\rangle \end{aligned}$$

we have

$$\begin{aligned} S_z|n\rangle &= (s-\hat{n})\,|n\rangle \\ &= (s-n)|n\rangle \end{aligned} \tag{20}$$

For $\boldsymbol{S}^2 = S_z^2 + \frac{1}{2}(S_+S_- + S_-S_+)$ we have

$$\begin{aligned} S_z^2|n\rangle &= (s-\hat{n})^2|n\rangle \\ &= (s-n)^2|n\rangle \\ S_+S_-|n\rangle &= \left(\sqrt{2s-\hat{n}}\right)\underbrace{bb^\dagger}_{1+\hat{n}}\left(\sqrt{2s-\hat{n}}\right)|n\rangle \\ &= (2s-n)\,(1+n)|n\rangle \\ S_-S_+|n\rangle &= b^\dagger\left(\sqrt{2s-\hat{n}}\right)\left(\sqrt{2s-\hat{n}}\right)b|n\rangle \\ &= b^\dagger\left(\sqrt{2s-\hat{n}}\right)\left(\sqrt{2s-\hat{n}}\right)\sqrt{n}|n-1\rangle \\ &= b^\dagger\,(2s-(n-1))\,\sqrt{n}|n-1\rangle \\ &= \sqrt{n}\,(2s-n+1)\,\sqrt{n}|n\rangle \\ &= n(2s-n+1) \end{aligned}$$

hence

$$\begin{aligned} \boldsymbol{S}^2|n\rangle &= \left(S_z^2 + \frac{1}{2}(S_+S_- + S_-S_+)\right)|n\rangle \\ &= \left((s-n)^2 + \frac{1}{2}\,(2s-n)\,(1+n) + \frac{1}{2}n(2s-n+1)\right)|n\rangle \\ &= s\,(s+1)\,|n\rangle \end{aligned}$$

The state $|n\rangle$ is thus an eigen state of $S_z$ and $\boldsymbol{S}^2$ with eigenvalues $m = s-n$ and $s(s+1)$ respectively. Therefore we have

$$|n\rangle = |s, m = s-n\rangle$$

For a spin $s$, the eigenvalues of $S_z$ must verify the constraint

$$-s \le m \le s$$

which is equivalent to

$$0 \le n \le 2s.$$