Exercise 1: The given variational state is,

$$|c\rangle = \frac{1}{\sqrt{2}}(|ab\rangle + c\,|ba\rangle)$$

The variational energy of the above state is given by:

$$\frac{\langle c|\,H\,|c\rangle}{\langle c|c\rangle} = \frac{(\langle ab| + c\,\langle ba|)\,H\,(|ab\rangle + c\,|ba\rangle)}{(\langle ab| + c\,\langle ba|)\,(|ab\rangle + c\,|ba\rangle)}$$

Substituting $\langle ab\,|ba\rangle = L^2,\ \langle ab|\,H\,|ab\rangle = V,\ \langle ab|\,H\,|ba\rangle = \langle ba|\,H\,|ab\rangle = X$:

$$\begin{aligned} E &= \frac{V + cX + cX + c^2V}{1 + cL^2 + cL^2 + c^2} \\ &= \frac{(1+c^2)V + 2cX}{1 + c^2 + 2cL^2} \end{aligned}$$

Finding the extrema of the above function:

$$\frac{\delta E}{\delta c} = 0 \implies c = \pm 1$$

Hence we have,

$$\begin{aligned} \psi_+ &= \frac{1}{\sqrt{2}}(|ab\rangle + |ba\rangle) \\ \psi_- &= \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle) \end{aligned}$$

with energies:

$$E_+ = \frac{V+X}{1+L^2}, \qquad E_- = \frac{V-X}{1-L^2}$$

Including the spin degrees of freedom and enforcing the anti-symmetry condition we obtain:

$$\begin{aligned} \psi_+ &= \frac{1}{\sqrt{2}}\,(|ab\rangle + |ba\rangle)\,(\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}) \\ \psi_- &= \frac{1}{\sqrt{2}}\,(|ab\rangle - |ba\rangle) \begin{cases} \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \\ |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \end{cases} \end{aligned}$$

Thanks to the anti-symmetry of the wavefunction (symmetric spatial term is a spin singlet, and antisymmetric spatial term is a spin triplet) we can map a pure Coulomb interaction (given by the spatial overlap terms of the orbitals expressed by L^2, V, X) in an *effective interaction of spins*. Here, there is not an *real* interaction between spins, but is the symmetry of the state that allows to switch between the two representations.
Now we need to understand how the operator $S_1 \cdot S_2$ acts on a triplet and a singlet state. From $S_{tot}^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2S_1 \cdot S_2$, then $S_1 \cdot S_2 = \frac{1}{2}(S_{tot}^2 - S_1^2 - S_2^2)$. S_1 acts only on the first spin, and knowing that its eigenvalues are $s(s+1)$ with $s = 1/2$, we get that $S_1^2 \to 3/4$. Same for S_2^2. S_{tot}^2 acts on the total spin of the singles ($s = 0$) or

triplet ($s = 1$) state, obtaining that $S_1 \cdot S_2 \to -3/4$ for the singlet, and $S_1 \cdot S_2 \to 1/4$ for the triplet. So the new effective Hamiltonian should give $H_{spin}\chi_{singlet} = E_+\chi_{singlet}$, and $H_{spin}\chi_{triplet} = E_-\chi_{triplet}$, and this can be obtained using the Hamiltonian

$$H_{eff} = \frac{1}{4}(E_+ + 3E_-) - (E_+ - E_-)S_1 \cdot S_2$$

and neglecting the constant term, the effective Hamiltonian can be written as

$$H_{eff} = -JS_1 \cdot S_2$$

with $J = E_+ - E_- = 2(X - VL^2)/(1 - L^4)$.

Exercise 2:

a) The first order correction is zero since operator T creates a double occupancy and hence the matrix element like $\langle\alpha\,|T|\,\beta\rangle$=0

b) The second order correction to the Hamiltonian is:

$$\begin{aligned}\langle\alpha|\,H^{(2)}\,|\beta\rangle &= \sum_\gamma \frac{\langle\alpha|\,T\,|\gamma\rangle\,\langle\gamma|\,T\,|\beta\rangle}{E_\alpha - E_\gamma} \\ &= \sum_\gamma \frac{\langle\alpha|\,T\,|\gamma\rangle\,\langle\gamma|\,T\,|\beta\rangle}{-U}\end{aligned}$$

the states $|\gamma\rangle$ correspond to states with single double occupancy. The dominator become U because the energy of the states $|\gamma\rangle$ is U due to the single double occupancy, while the states $|\alpha\rangle$ have zero energy for the selected ground state hamiltonian.

If we write T explicitly we get:

$$\langle\alpha|\,H^{(2)}\,|\beta\rangle = -\frac{t^2}{U}\sum_\gamma \langle\alpha|\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\,|\gamma\rangle\,\langle\gamma|\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\,|\beta\rangle \tag{1}$$

The outer sum is only over γ so it can be brought inside the expression, giving:

$$\begin{aligned}\langle\alpha|\,H^{(2)}\,|\beta\rangle &= \frac{t^2}{U}\langle\alpha|\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\sum_\gamma|\gamma\rangle\,\langle\gamma|\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\,|\beta\rangle \\ &= -\frac{t^2}{U}\langle\alpha|\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\mathbf{I}\sum_{ij\sigma} c^\dagger_{i\sigma}c_{j\sigma}\,|\beta\rangle \\ &= -\frac{t^2}{U}\langle\alpha|\sum_{ij}\sum_{\sigma\sigma'} c^\dagger_{i\sigma}c_{j\sigma}c^\dagger_{j\sigma'}c_{i\sigma'}\,|\beta\rangle\end{aligned}$$

Here we reconcile the two summations by including the indices σ and σ', denote spin up or down and we swap j and i on the first two operators so that, if $\sigma = \sigma'$, the result of the whole operation is to move an electron from one sight and then move it back to the same sight.
Therefore, in terms of fermionic creation and annihilation operators this can be written as:

$$H^{(2)} = -\frac{t^2}{U}\sum_{ij}\sum_{\sigma\sigma'} c^\dagger_{i\sigma}c_{j\sigma}c^\dagger_{j\sigma'}c_{i\sigma'} \tag{2}$$

c) Considering $\{|\alpha_{\uparrow\uparrow}\rangle, |\alpha_{\uparrow\downarrow}\rangle, |\alpha_{\downarrow\uparrow}\rangle, |\alpha_{\downarrow\downarrow}\rangle\}$ as vectors of a space, the matrix element between these states becomes:

$$\langle\alpha_{\sigma_1\sigma_2}| H^{(2)} |\alpha_{\sigma_3\sigma_4}\rangle = -\frac{t^2}{U}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

which can be rewritten as:

$$\begin{aligned} \langle\alpha_{\sigma_1\sigma_2}| H^{(2)} |\alpha_{\sigma_3\sigma_4}\rangle &= \frac{2t^2}{U}\left[\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{pmatrix} - \frac{1}{4}\right] \\ &= \frac{2t^2}{U}\left(S_i \cdot S_j - \frac{1}{4}\right) \end{aligned}$$

Since each atom has two neighbours, summing over the possible interactions obtains:

$$\langle\alpha| H^{(2)} |\beta\rangle = \frac{4t^2}{U}\sum_{<i,j>}\left(S_i \cdot S_j - \frac{1}{4}\right)$$