Author: Noore Elahi Shaik
Please send any suggestions/corrections to **noore.shaik@epfl.ch**

Exercise:1

a) Using second order perturbation with a hopping term $T = t_{pd}p^\dagger d + H.C$ the effective hopping between state $|\alpha\rangle$, where an electron occupies a particular Cu site, to $|\beta\rangle$ where the electron occupies the adjacent Cu site.

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

the states $|\gamma\rangle$ correspond to states with one electron on the oxygen atom between the Cu sites. This state is Δ_{CT} higher in energy when compared to the initial state. Using the same analogy as Exercise-2.2 we obtain the effective hopping energy as,

$$t_{dd}^{eff} = \frac{t_{pd}^2}{\Delta_{CT}}$$

b)The given process can be effectively translated to hopping between the d orbitals

$$d_i^n p^6 d_j^n \rightarrow d_i^{n-1} p^6 d_j^{n+1} \rightarrow d_i^n p^6 d_j^n$$

with effective dd hopping as obtained in part 'a'. Using the result from Exercie -2.2 we have

$$J_{dd}^{(1)} = \frac{2t_{dd}^2}{U_{dd}} = \frac{2t_{pd}^4}{\Delta_{CT} U_{dd}}$$

c) A similar calculation as above, would provide us with the coupling. The intermediate state $d^{n+1}p^4d^{n+1}$ is $2\Delta_{CT} + U_{pp}$ above the initial and final state. Also, there are two possible exchange paths, one in which the holes return to their respective site, the other one with the holes interchanging their site positions. Hence the total contribution becomes:

$$J_{dd}^{(2)} = \frac{4t_{pd}^4}{\Delta_{CT}^2(2\Delta_{CT} + U_{pp})} = \frac{2t_{pd}^4}{\Delta_{CT}^2(\Delta_{CT} + \frac{U_{pp}}{2})}$$

d) The total Heisenberg exchange coupling is given by:

$$J_{total} = \frac{2t_{pd}^4}{\Delta_{CT}^2}\left(\frac{1}{U_{dd}} + \frac{1}{\Delta_{CT} + \frac{U_{dd}}{2}}\right)$$

We observe that for a Mott Hubbard insulator $\Delta_{CT} >> U_{dd}$ the first term dominates and the lower charge excitations are primarily between d shells. For a charge transfer regime $U_{dd} >> \Delta_{CT}$ we observe that second term dominates and the low level excitations would be primarily the ones that involve excitations between p and d orbitals.