Charge analysis based on number of electrons on P- and N- doped LaMnO3

- LaMnO3 => La^{3+}; Mn^{3+}; $O_3{}^{2-}$ - charge distribution.
- La3+ has 8 valence electrons; Mn3+ has 4 valence electrons; and O2- has 8 valence electrons. (=>$O_3{}^{2-}$ has 24 valence electrons); thus **one unit** of LaMnO3 has **36 valence electrons.**
- In the present case, the simulations are done on a 4x4x4 supercell; thus implying a total of (36*64) = 2304 valence electrons.(shown rightly in Bader charge analysis).
- Precisely, La = 64*8 = 512; Mn = 64*4 = 256; O = 64*3*8 = 1536 valence electrons.

P-Doping

- P is substituted on the Mn site in systematically small amounts; starting from P=1 to P=7.
- Considering the case P=1: one P atom substitutes on the Mn site.
- P has 5 valence electrons; substituting 1 P to replace one Mn atom reduces the total valence electron number on Mn by 2. (**This is seen in 'mag' in VASP output**); thus indicating that P assumes 3+ state (2 valence electrons) thus replacing one Mn (4 valence electrons) (-4+2 = -2) => number of Mn valence electrons to 254. (hence the total valence electrons to 2302)
- Similarly, with more P concentration, the Mn valence electrons (and hence charge) reduces @2 per P atom.
- The net magnetisation on Mn stays app. 4 indicating a d4 spin state.

N-Doping

- N is substituted on the O site, again in very small amounts; starting from N=1 to N =11.
- Considering N=1; one N atom substitutes on O site.
- N has 5 valence electrons; therefore, N2- has 7 valence electrons; O2- has 8 valence electrons.
- This means that for each N substitution on the O-site; the total electrons should reduce by 1. (-8+7).
- This is again observed from 'mag' in VASP output, that for each N substitution, the 'mag' value reduces by 1.
- The net magnetisation on Mn still remains 4 i.e. a d4 state.

Proposition

- It is thus seen that for both P and N substitution, the effect of charge compensation is seen on the Mn atom.
- However, the net valency on Mn still remains 3+ for both P and N substitutions.
- This contradicts the initial presumption that P and N doping should have counter-effects on Mn valency, thus cancelling the net magnetisation.
- Question: Should P and N be continued for site substitutions or other elements that have higher number of valence electrons in the respective oxidation states should replace?
- This does not really refrain from studying the surface catalytic properties using P and N, specially given that experimental results are promising. (?)

- These then decide the next steps in this context.

*P.S: The charge density plots of course do not coincide with this theory yet, but I think that's because there is some problem with the plotting itself and not with data. I will look into it.

Number of P-atoms on Mn site	**mag**
1	254
2	252
3	250
4	248
5	246
6	244
7	242

Number of N-atoms on O site	**mag**
1	255
2	254
3	253
4	252
5	251
6	250
7	249
8	248
9	247
10	246
11	245

Bader Analysis

- Important to note that Bader analysis indicates the charge distribution within a system.
- The ‘charge’ column in the Bader.dat file indicates the charge on atoms at each site.
- Precise description of Bader charge calculation is found on the link (http://henkelmanlab.org/forum/viewtopic.php?t=769)
- For example, we take the first charge entry on P1.dat (given in repository).
- This value corresponds to the charge on the first La atom of the system (POSCAR file).
- **This shows a charge = 8.906009. Now, as mentioned previously, La has a 3+ oxidation in LaMnO3; meaning 8 valence electrons. Subtracting 8 from the charge value, => 8.906-8 = 0.906 ~ 1 electron is transferred from La to the system**.
- The charge on O = 7.298; subtracting from the valence electrons 8; one gets 0.7 ~ 1; meaning oxygen gets the electron transferred from La (since oxygen is electronegative).
- Similarly, in same file, the charge on P is shown 0.00000. P3+ has 2 valence electrons; again implying that 2 electrons are transferred to the system from P.
- This matches with the previous proposition that P transfers 2 electrons to Mn; thus adjusting the Mn valency.