When we use PBE approach to estimate the exchange correlation energy term in the Kohn Sham Equations, the band gaps obtained as a result are usually underestimated(in fact, the result for a semiconductor may come out to be a metal(0 band gap)). The reason for this is that the Density Functional Theory was formed in order to find ground state properties of the system, whereas band gap is an excitation state property(properties that describe the behavior of the system at an excited state). More specifically, a *missing derivative discontinuity term* in the PBE functional(This problem occurs also in many other DFT functionals) accounts for this underestimation.

Numerically, PBE approach to estimate the exchange correlation energy undermines the Band gap less than other LDA functionals. The mean absolute error is 0.9eV, with a mean percentage error of -42%.

Performing SCF calculations involves iteratively solving the Kohn Sham equations with different electron densities each time. This does correctly imply that there are different number of electrons in the system. In literature, sometimes this is misinterpreted as the system having a net charge density. This would mean that the system has infinite energy as, in simulations, the unit cell is assumed to mean an infinite crystal. A net charge in a unit cell would translate to infinite charge in the entire crystal and hence infinite energy(1).

LDA and GGA are known as **Semi local functionals.**

As electrons are added to the system in each iteration, the exchange correlation effects (also other properties) change significantly. Hence as the number of electrons increases, the exact functionals also change in a similar manner and there is hence a discontinuity in between the integer (number of electrons). Although the number of electrons can also be non integers in some cases, integral number of electrons in a system is more common and the discussion here would remain same. The approximate Functionals that are used to estimate the complex exchange correlation effects aren't able to capture this discontinuity and the underestimation in Band gap is broadly due to this reason. This discrepancy is known as "***Derivative Discontinuity***" since the derivative of the exact exchange correlation function is large in between two integers(1).
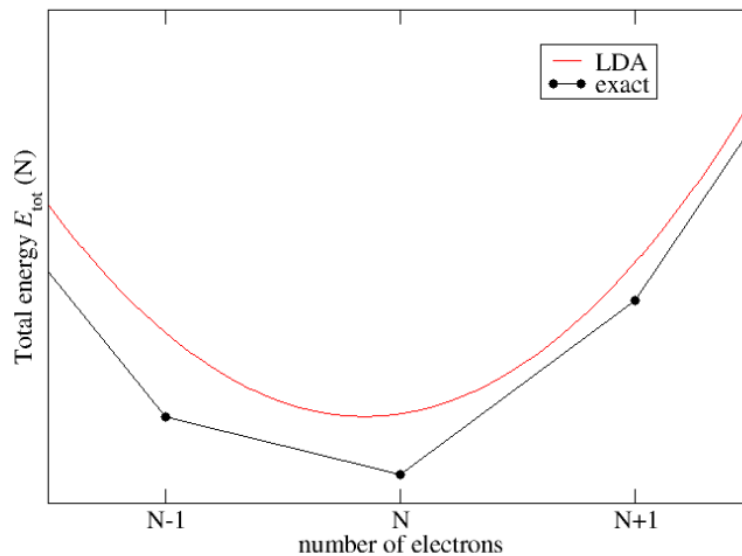
Another reason for the underestimation of band gap is the **"Self interaction error".** This error arises when an electron interacts with itself due to the potential it created. This, in theory, should cancel out but in approximate methods, it does not. As a result when we use LDA and GGA to approximate the exchange correlation functionals, this self interaction error causes the occupied states to be over-localized(spread out more than they should be). As a result their energy is increased, and this causes a decrease in the band gap(1).

In the Hartree-Fock Theory this Self Interaction Error affects the unoccupied states and and they get occupied as a result of which their energy increases. Hence the Band gap increases.

The Self Interaction error can be solved by mixing semi local functionals(LDA and GGA) and F*ock operator* (essentially combine the two theories).

Sources