Boron nitride is a promising candidate as a dielectric layer in 2D-material based devices [1]. Bulk hexagonal boron nitride (hBN) is isostructural to graphite, forming a layered honeycomb structure where boron and nitrogen atoms are held together by strong sp² bonds, giving hBN excellent mechanical strength and chemical stability [2,3]. Likewise, single layer hBN is also isostructural with graphene. Unlike graphene, however, single layer hBN is an insulator with a nonzero band gap between 5 and 6 eV [4].

In devices, semiconductor function is affected by the presence of intrinsic defects. For example, it is known that oxygen vacancies in semiconducting oxides (SiO₂, HfO₂) are linked to the filament formation process in resistive RAM devices [5,6]. Studies [7] have shown boron vacancies to be related to the analogous breakdown process in multilayer hBN.

Here we present the results of our investigation into hBN and a collection of its intrinsic defects. Using density functional theory (DFT), we analyse a range of defects in hBN, including boron and nitrogen vacancies, interstitials and Stone-Wells defects. We present the charge transition levels (CTLs), the ground state spin configuration, and the formation energies of the defects.

We use the CP2K software package [8] to implement DFT. This uses a Gaussian type atomic centred basis set and calculates electronic structure in the gamma point. We use a hybrid-DFT functional to calculate exchange and correlation energies. The calculations use 6x6x4 supercells in periodic boundary conditions. This particular cell expansion was used to give an effective K-point spacing which would sample the HOMO and LUMO states [9].

The CTLs of the intrinsic defects are calculated and, by alignment with typical electrode workfunctions, it is found that a number of intrinsic defects can be charged during device function. Divacancies are found to have positive binding energy. In particular, the formation of a "molecular bridge" in interlayer divacancies increases their stability. For example, in the lowest energy configuration of an interlayer boron divacancy, two N atoms form a N-N bridge across the layers. This greatly deforms the surrounding structure and reduces the energy required to form a boron vacancy-interstitial pair. The structure and dynamics of such defects may play a significant role in the breakdown of hBN in nanoelectronic devices.