

Characterization of (BN)_n Cage Emission Band Gaps exploiting Massively Parallel Analytical TDDFT Gradients

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Introduction

The III-V nitrides form an important family of medium to wide band gap semiconductors. The family includes well known semiconductors such as GaN and InN but also less well understood materials such as BN. Due to the similarity between B-N bonds and C-C bonds boron nitride can form phases similar to carbon. For example, it can form a layered hexagonal phases similar to graphite and a cubic zinc-blende phase similar to diamond. In addition the material can form cage structures similar to Buckminsterfullerenes. These cage structures are interesting as they offer their size as an additional parameter that may be exploited to tune their properties. Although the structures are similar to those of carbon they are not the same because they are made up of two elements boron and nitride and the fact that B-N bonds are favoured over B-B and N-N bonds. The consequences of this are immediately obvious in the cage structures. Unlike the 5- and 6-rings that appear in carbon cages the boron nitride cages show only 4- and 6-rings. It is also apparent in the properties in that whereas carbon cages are semi-metals boron nitrides are semi-conductors due to their partially ionic character. Because of their potential for Light Emitting Diodes (LED) in the UV domain and converse for photovoltaic cells a closer look at these clusters is warranted.

Initially we look at simple clusters such as (BN)₅, (BN)₆, (BN)₁₂, and (BN)₁₆ in "perfect" structures. In future work we plan to look at the influence of defects as well. To characterise these clusters we investigated their spectra [1] for which we used TDDFT with the PBE functional. The method was chosen to allow studying much larger systems, such as (BN)₁₀₀ later on.

TDDFT Gradients

The spectra of molecules and clusters can be calculated within TDDFT. However to study changes of the structure upon excitation it is necessary to evaluate the gradient in the excited state. Using finite differences for this purpose is viable for small systems only. For many atom systems analytical gradients are required. The formalism for this property has recently been developed and implemented in Turbomole [2]. To study the systems of interest to us it is desirable to employ a substantial number of processors to reduce the elapse time of the calculations. With this in mind we chose NWChem [3] as a development platform for a massively parallel implementation of the TDDFT gradients as this code has all the infrastructure to target the required machines.

The final expression for the gradient is

$$\Omega^{\lambda} = \sum_{\mu\nu\sigma} h_{\mu\nu\sigma}^{\lambda} P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} S_{\mu\nu\sigma}^{\lambda} W_{\mu\nu\sigma} + \sum_{\mu\nu\sigma} Y_{\mu\nu\sigma}^{\lambda} P_{\mu\nu\sigma} + \sum_{\mu\nu\sigma\tau} (\mu\nu|\tau\nu)^{\lambda} \int_{\mu\nu\sigma\tau} P_{\mu\nu\sigma\tau} + \sum_{\mu\nu\sigma\tau} f_{\mu\nu\sigma\tau}^{\lambda} (X+Y)_{\mu\nu\sigma\tau} (X+Y)_{\tau\mu\sigma\tau}$$

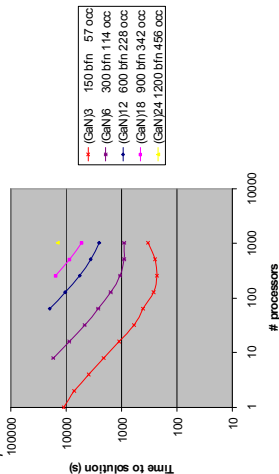
$$P_{\mu\nu\sigma} = T_{\mu\nu\sigma} + Q_{\mu\nu\sigma}$$

This is remarkably similar to the expression for the gradient of the ground state. The only completely new term is the one involving vectors (X+Y) from the TDDFT calculation. Of course there are TDDFT contributions hidden in the quantities P, W, and Γ but provided these are coded sensibly the ground state gradient machinery can be used with little modification. In the formulation the Z-vector method is used to arrive at the relaxed density matrix P. This has the advantage that only one linear system of equations needs to be solved instead of one for every atomic coordinate. However as P is independent of the type

of perturbation it may be used to calculate properties other than the gradient as well.

In implementing this functionality in NWChem we build on the infrastructure already in place. This means we could reuse the TDDFT matrix-vector multipliers, the ground state gradient machinery and the components offered by the Global Arrays such as matrix multiplication. This meant that the code could be implemented with relatively little coding of specific terms and the parallelism was obtained almost for free. The resulting implementation was evaluated at the LDA level using gallium nitride clusters on the Daresbury BlueGene/L system. The results shown in figure 1 show that the gradient code scales up to 1024 processors from 600 basis functions onwards.

Figure 1: Parallel scaling of the TDDFT gradient implementation



derivatives we are redesigning the repository to address these issues [4]. The current plans are to move to a modular approach in which the library will provide a collection of functionals, mechanisms to select and combine them, as well as query them with respect to important characteristics. At this stage any input from potential users and developers is welcome and can be sent either directly to me or added to the project wiki [4].

Results

With the code we have developed we have now started to look at phenomena in the excited state involve a wider knowledge of the excited state potential energy surface than just a single point. One question is whether the boron nitride clusters we looked at before are actually stable in the excited state and how their spectra change as the cluster relaxes in the excited state. For this purpose the spectra at the ground state equilibrium geometry and the first excited state equilibrium geometry were calculated with the PBE

Figure 2: Change of spectrum upon excitation for (BN)₃

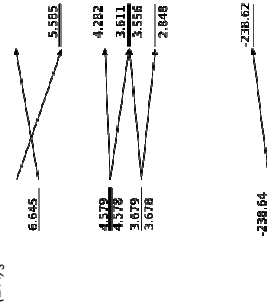
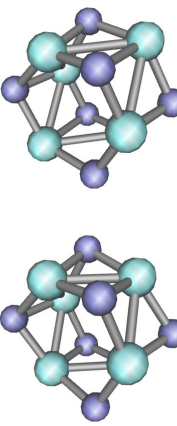
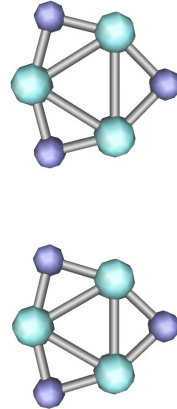
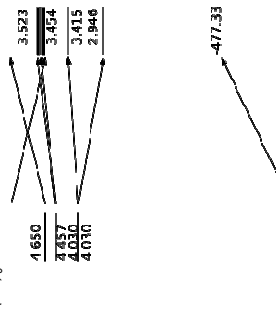


Figure 3: Change of spectrum upon excitation of (BN)₆



DFT Repository

An important issue in evaluating the TDDFT gradients is the presence of factors such as $f_{\mu\nu\sigma}^{\lambda}$, which involve third order partial derivatives of the density functionals. Implementing these is potentially a massive task. Depending on the level of functional the number of parameters can range from 2 for LDA to 9 for meta-GGA functionals. This means there may be 4 to 165 third order partial derivatives. Already during a former project implementing the DFT Hessians it was realized that deriving these partial derivatives by hand was unpractical and some automatic way is required. Also re-implementing these derivatives for different codes is pointless. It makes much more sense to go through this exercise once and have a library of routines that provide the required functionals for whoever wants them. This was the basic idea behind the DFT repository.

In this repository there was a separate routine for every supported functional. One of the advantages was that every published functional could closely match an author's work even if authors for example disagreed on the number of digits to use for fundamental constants. Another advantage was that developers could just hand pick the functionals they were interested in without having to pick up all the others as well.

There were also some serious disadvantages. One of them was that there was no mechanism to construct custom functionals from the terms available. Also there was no mechanism to query a functional about its properties, for example to find out if it was an LDA or GGA functional. More seriously this also meant that there was no way to incorporate the fraction of Hartree-Fock exchange that had to be added to hybrid functionals. In the light of rebuilding the repository to incorporate the partial third order

cluster at 0.83 eV. Another aspect of the spectra of these clusters is that there are a number of degenerate excited states. At the ground state equilibrium geometry this might follow from the symmetry of the clusters. Nevertheless even at the distorted geometries that correspond to the excited state equilibrium geometry many degeneracies remain.

Conclusion

We have developed a scalable parallel TDDFT gradient code which for which we have demonstrated scaling up to 1024 processors on a BlueGene/L system. This code has been applied to the investigation of the effect of structural relaxation of boron nitride clusters in the excited state. The preliminary results presented show that the clusters are stable in the excited state, with very limited change to structure occurring. The spectra do change significantly with (BN)₆ showing a more pronounced change than (BN)₃.

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