

Ab initio studies of vacancy-impurity complexes in cubic and hexagonal diamond

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Ab initio studies . . .



Hello my name is Alejandro and I am currently working on my master thesis project entitled:

Ab initio studies of vacancy-impurity complexes in cubic and hexagonal diamond

The supervision of the project is conducted by Dr. Andreas Grueneis , head of group at the MPI for solid state research. We engaged in this project as a joint collaboration with the third physical institute of this University, which is led by Prof. Joerg Wrachtrup.

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Ab initio studies ...

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Summary and outlook

In the following we will provide some basic background in the field of vacancy-impurity complexes and we will quickly introduce some of the techniques used to model and calculate their electronic properties.

The main systems of this work will be introduced and we will finish by giving a quick outlook into the possible future directions that this research could be led into.

Aim and scope of the work

Aims

- Exploration of defect centres using state-of-the-art ab-initio theories.
- Reproduce and obtain classical results for nitrogen vacancy impurity complexes in diamond.

Ab initio studies ...

└ Aim and scope of the work

└ Aims

- Exploration of defect centres using state-of-the-art ab initio theories.
- Reproduce and obtain classical results for nitrogen vacancy impurity complexes in diamond.

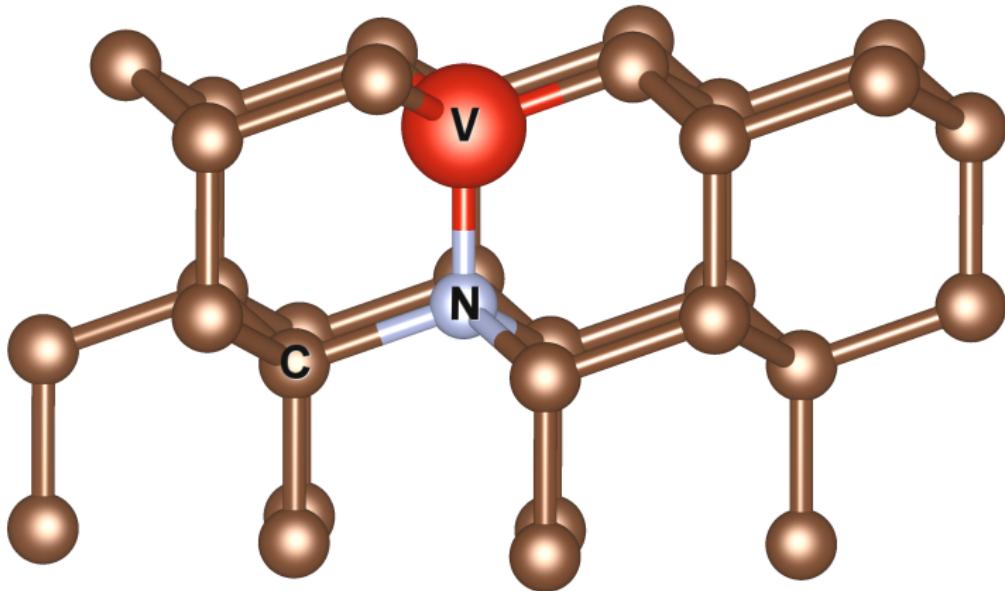
So the main aim of this work is to computationally treat electronic properties of defect centers in diamond using state-of-the-art ab initio theories.

Through this exploration we hope to recover many well-known experimentally verified quantities.

In order to do this we use several purely theoretical results to orient our calculations into the right direction. (e.g. Markus' Gruppentheorieberechnungen)

Introduction

Nitrogen Vacancy Centre in diamond (NV center)

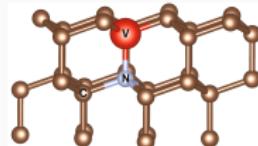


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Ab initio studies ...

└ Introduction

└ Nitrogen Vacancy Centre in diamond (NV center)



So let us just begin by firstly introducing the main actor in this story.

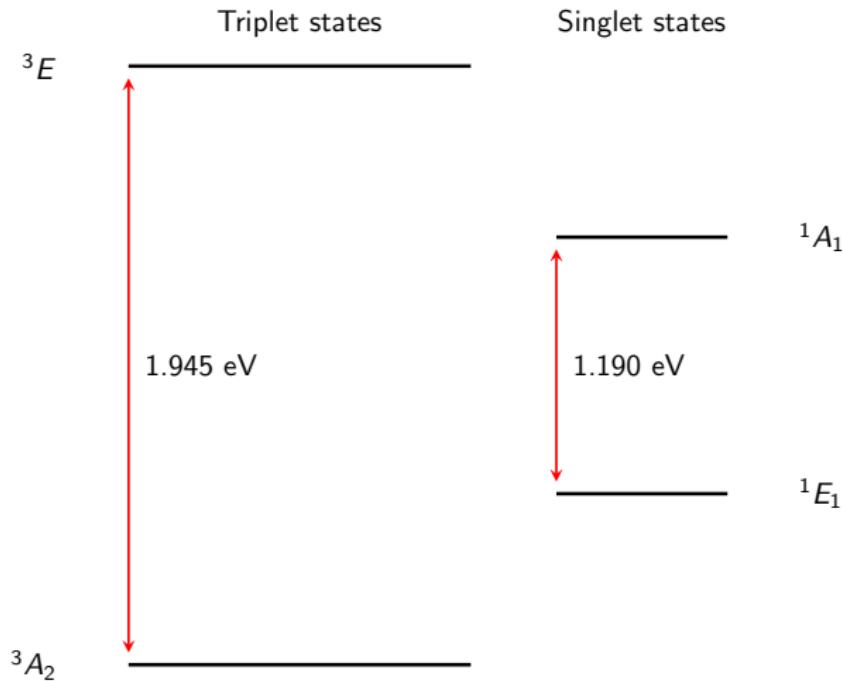
This is the Nitrogen vacancy impurity center in diamond, as most of you may already know. The big red region is a vacant carbon site and next to it lies a nitrogen atom.

This kind of defects has been researched now for almost 50 years.

However it was not until the late nineties when single negatively charged NV centres where found. This enabled the demonstration of photo stable single photon emitters, which is of course of huge importance for quantum optics.

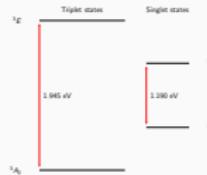
The most notable and studied of the NV centers is the negatively charged one.

Main level overview: NV⁻



Ab initio studies ...

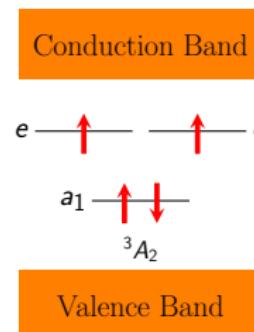
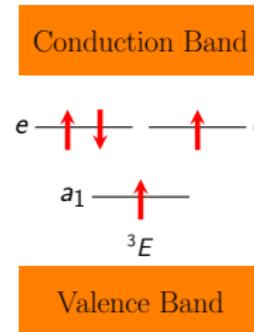
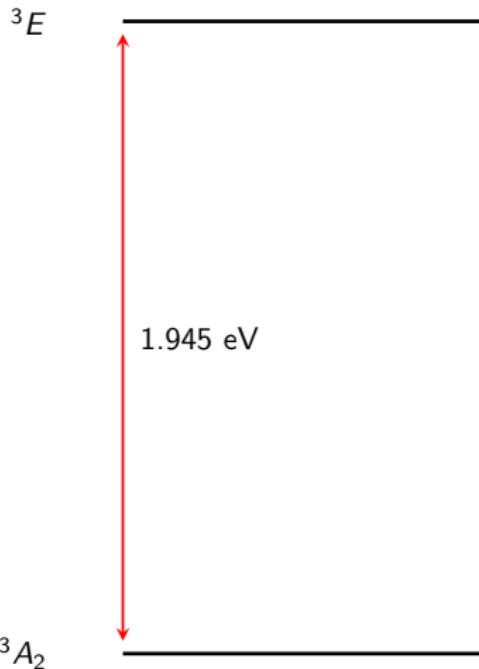
└ Introduction

└ Main level overview: NV⁻Main level overview: NV⁻

To explain fluorescence experiments it is essential to have a picture of the electronic and vibronic states of a defected diamond sample. Theoretical models using a *Linear combination of atomic orbitals* (LCAO) give rise to a good prediction of the Spin multiplicity and triplet energy levels of the negative NV center.

From the interplay of theory and experiments arises this electronic level scheme. On the one hand we encounter two stable triplet levels, where one of them is the ground state of the defect. Between them lie two metastable singlet states, which will play an essential role for applications of the defect levels.

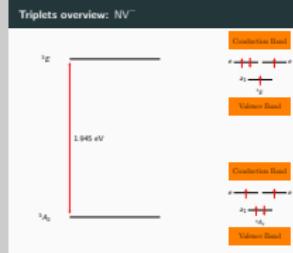
Triplets overview: NV⁻



Ab initio studies ...

└ Introduction

└ Triplets overview: NV⁻



If you have never heard of this defect before, you might be wondering how exactly the electrons in the solid body come into play. In the one particle picture of the problem it turns out that we can characterise very well these levels by the occupation of the valence states in the body.

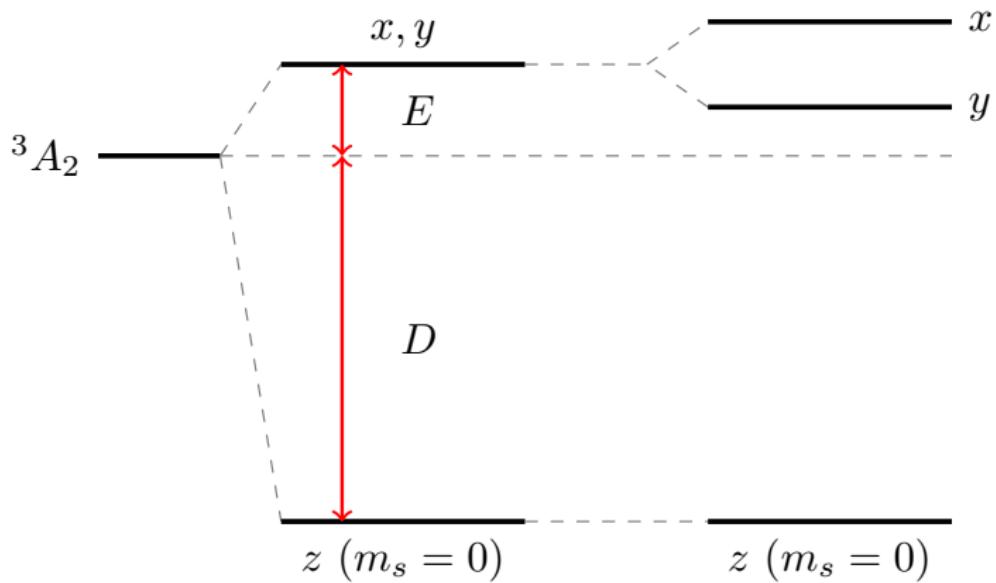
In this picture we can associate to every state with an occupation of the topmost states. From this picture we can see that the total spin is one and the excitation happens through the promotion of one electron in the level a_1 into one of the degenerated e levels. This without incurring in a spin flip process.

This we should also find in our calculations.

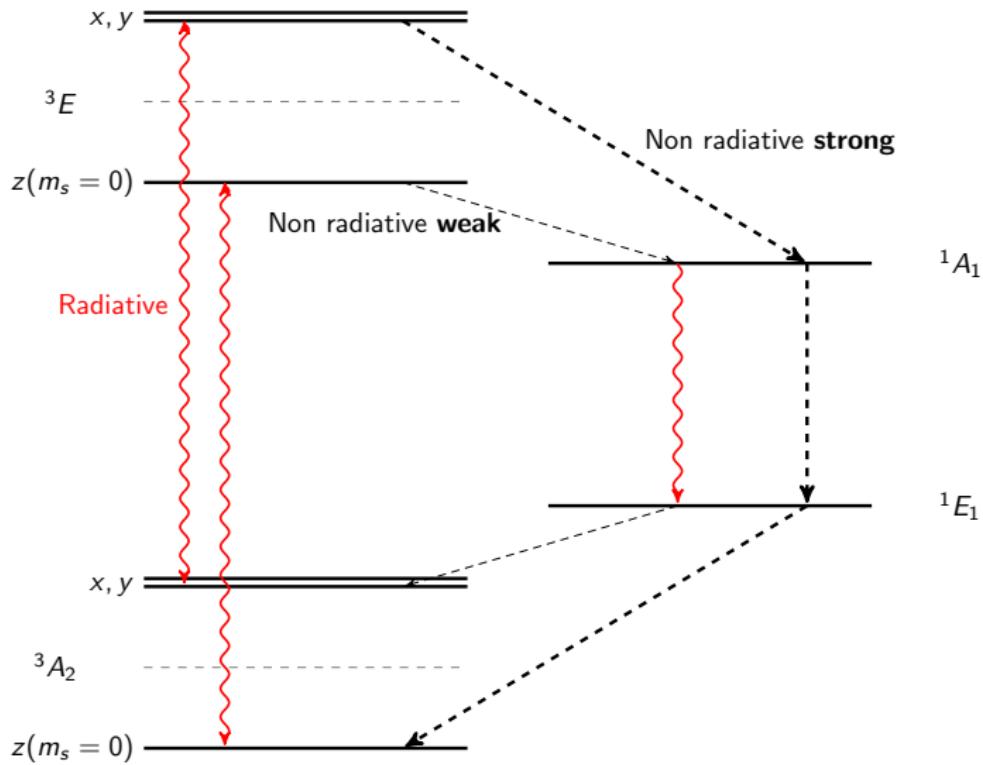
Transitions

$\hat{\mathbf{S}}^t \mathbf{D} \hat{\mathbf{S}}$

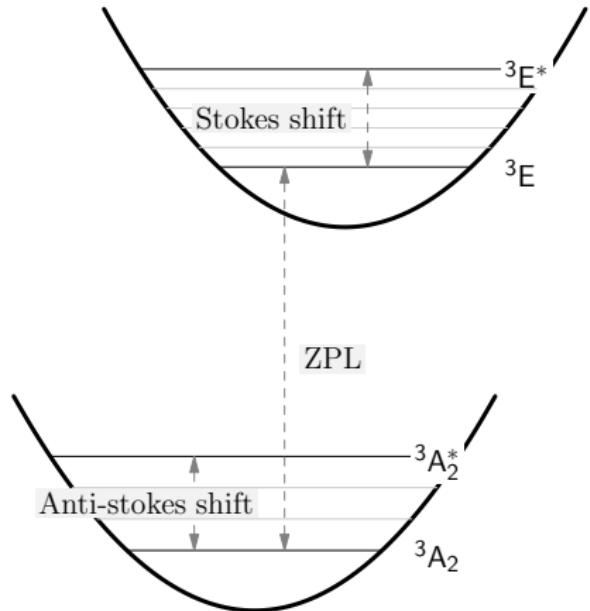
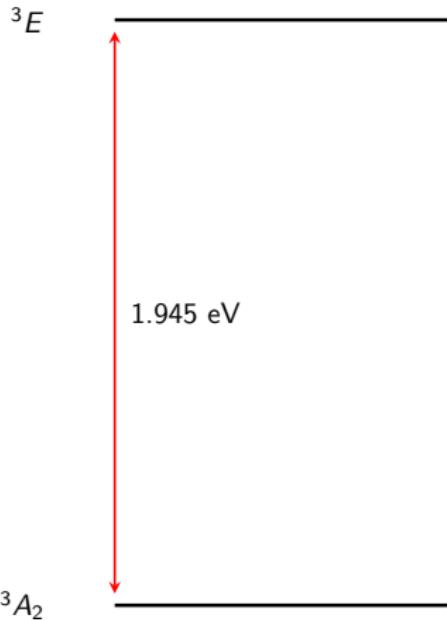
Zeeman/strain



Transitions overview: NV⁻



Zero phonon line (ZPL)



Density functional theory (DFT)

“ Ψ contains too much information”

- Popular saying

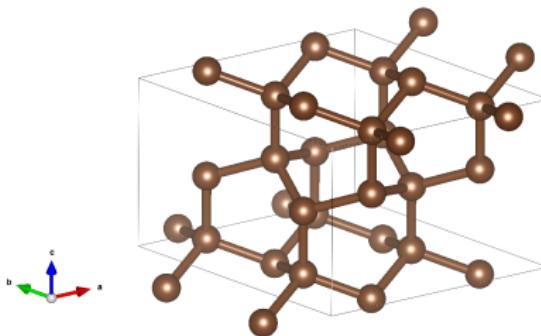
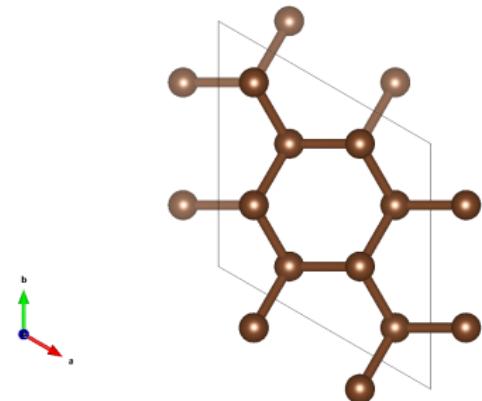
- The exact electronic ground state of a system is only dependent on the electronic density ρ .
- In principle, DFT delivers the **exact ground state**.
- All quantities written in terms of ρ (functional formalism).
- E.g.:

$$E[\rho] = T_s[\rho] + \int V(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}^{\text{exact}}[\rho]$$

The exchange correlation potential $E_{\text{xc}}^{\text{exact}}[\rho]$ determines the DFT flavor. In many calculations we use the so-called **PBE** (*Perdew-Burke-Ernzerhof*) functional.

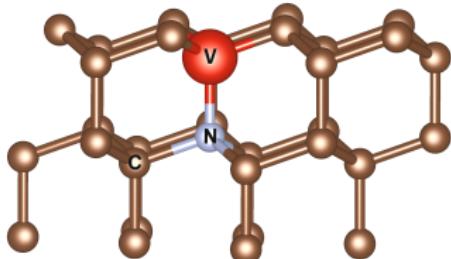
Hexagonal diamond and defects

Hexagonal diamond

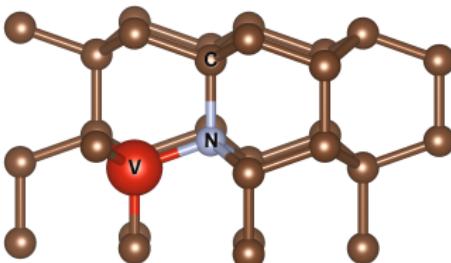


Defected hexagonal diamond

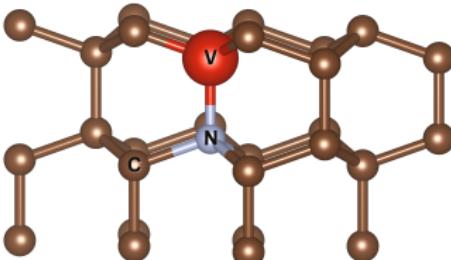
Cubic diamond



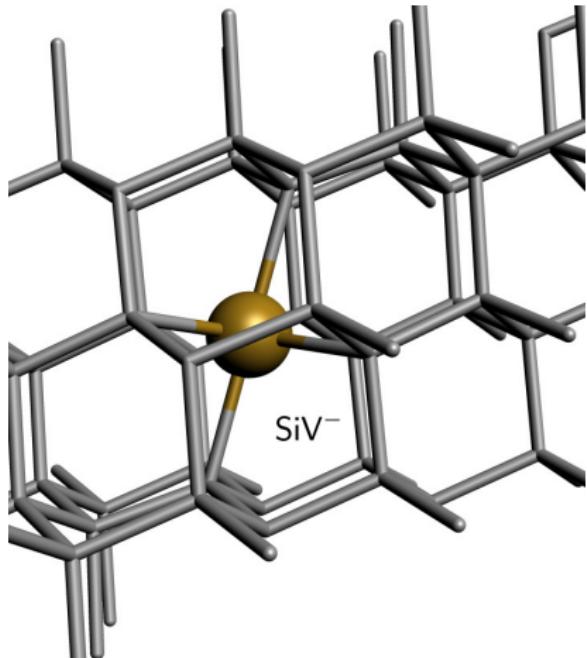
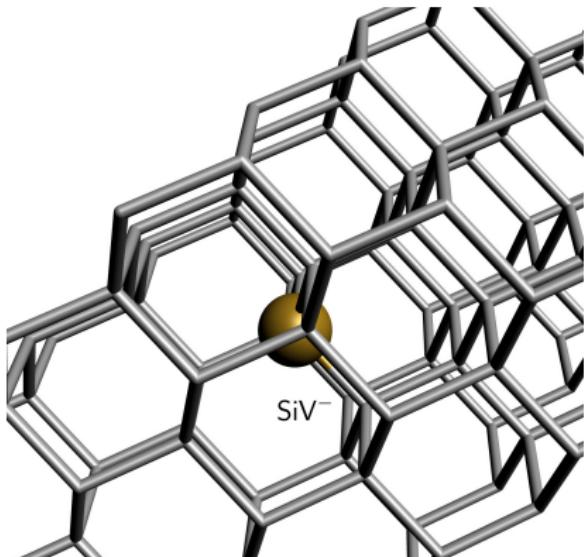
Hexagonal x-type



Hexagonal z-type

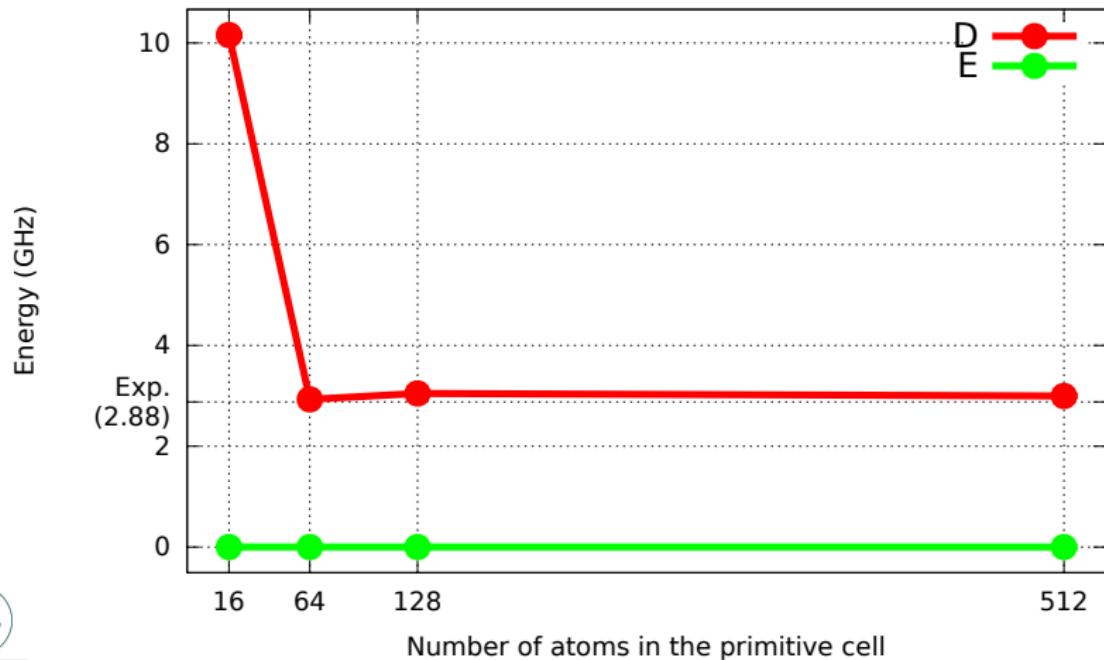


Split vacancies: SiV⁻

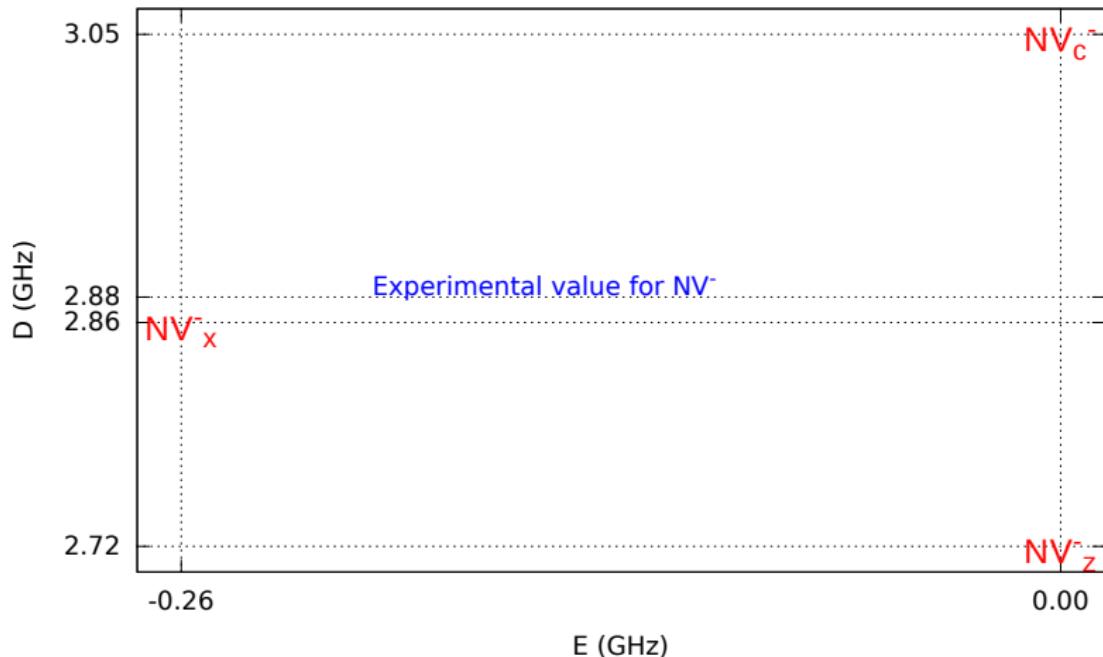


Results

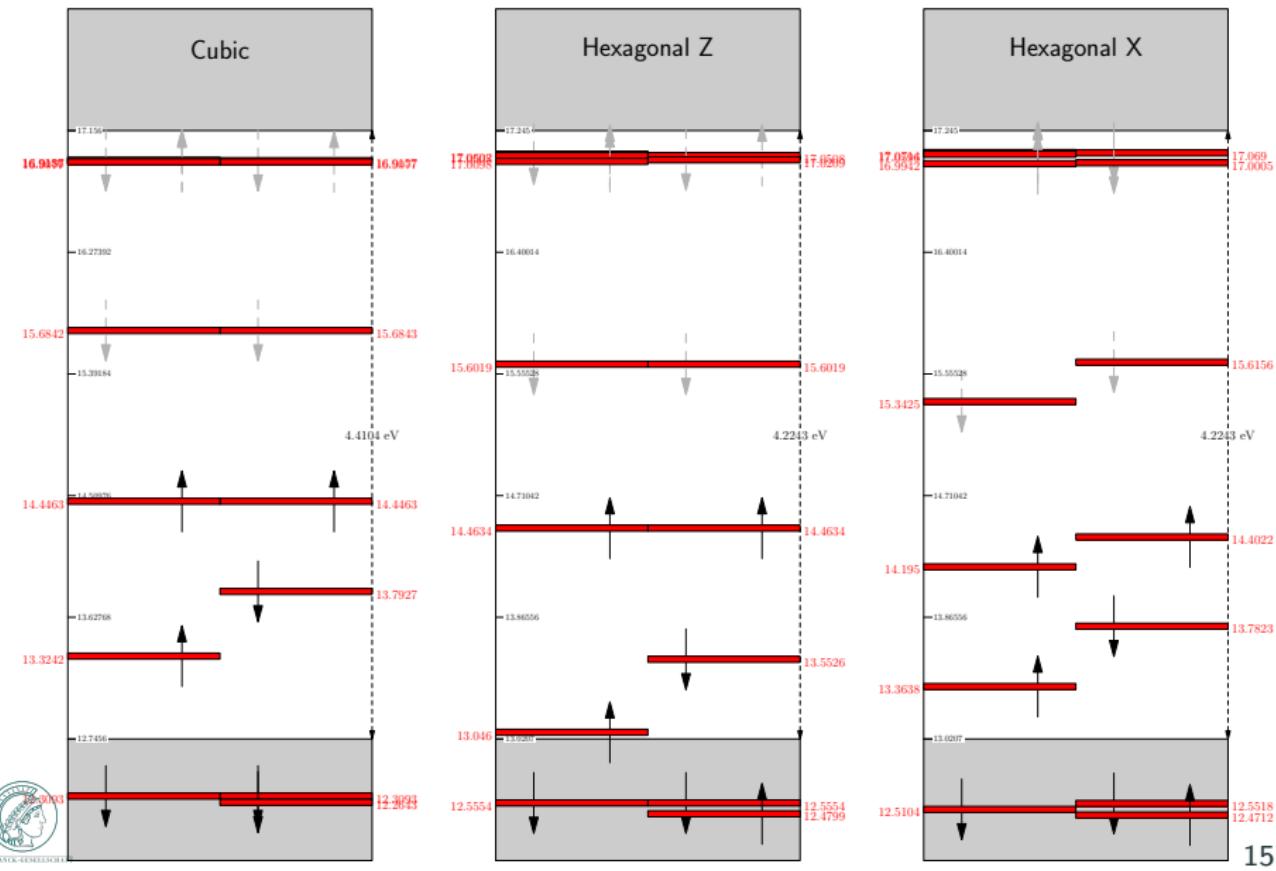
- Cubic diamond, convergence and comparison with the experimental result.



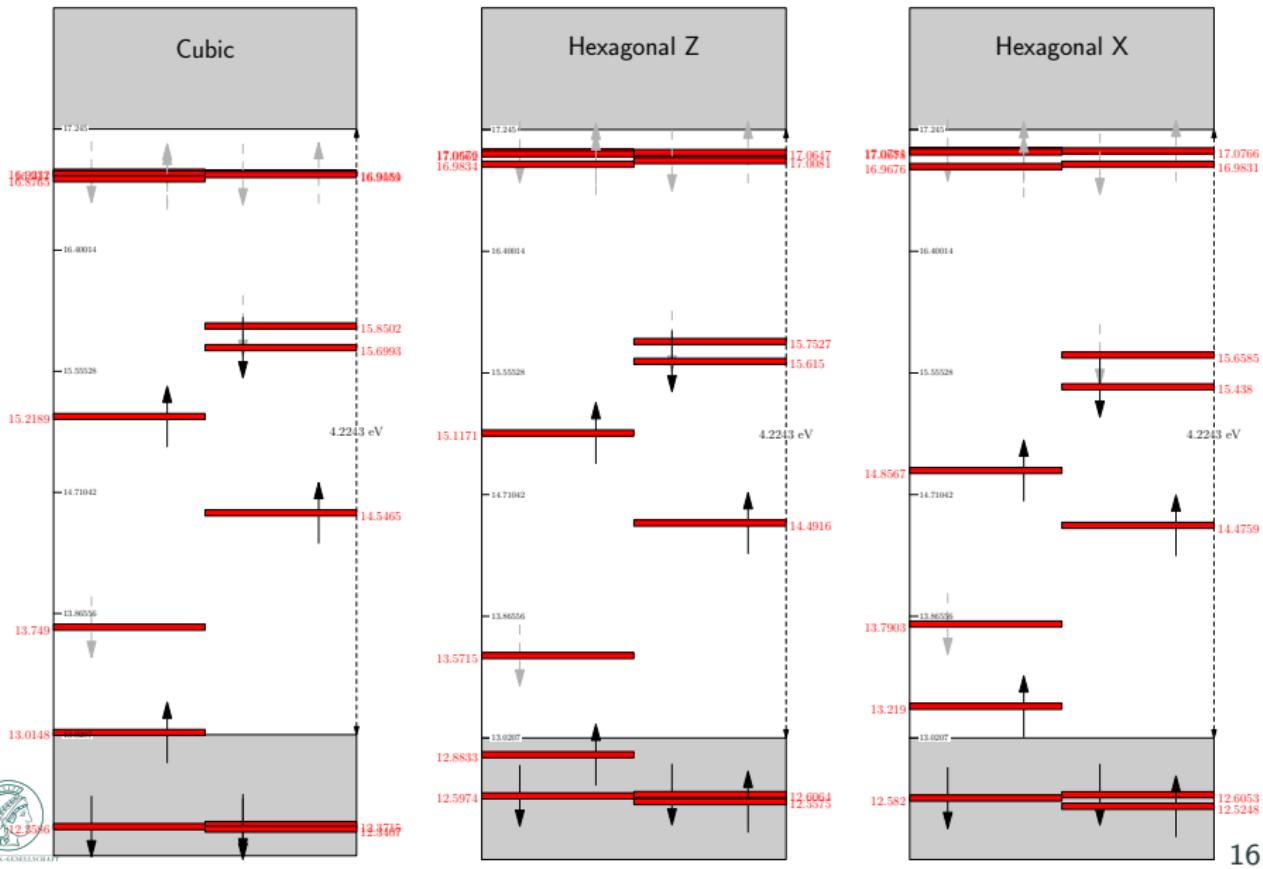
NV*: ZFS cubic (NV_c^*), Hexagonal x, z ($NV_{x,z}^*$)



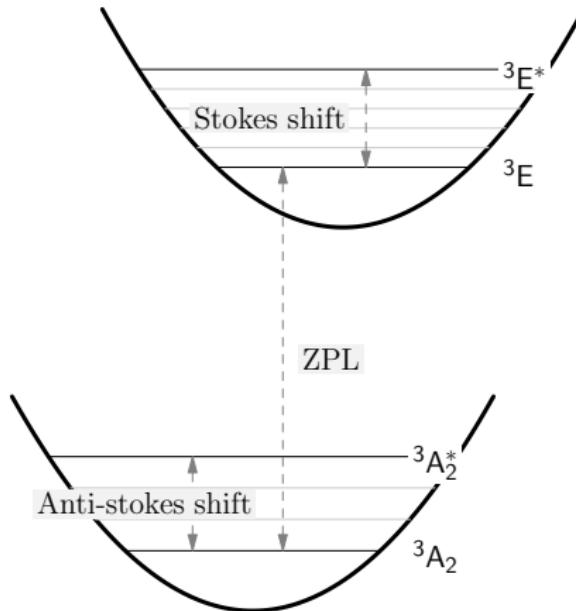
NV⁻: Ground state 3A_2



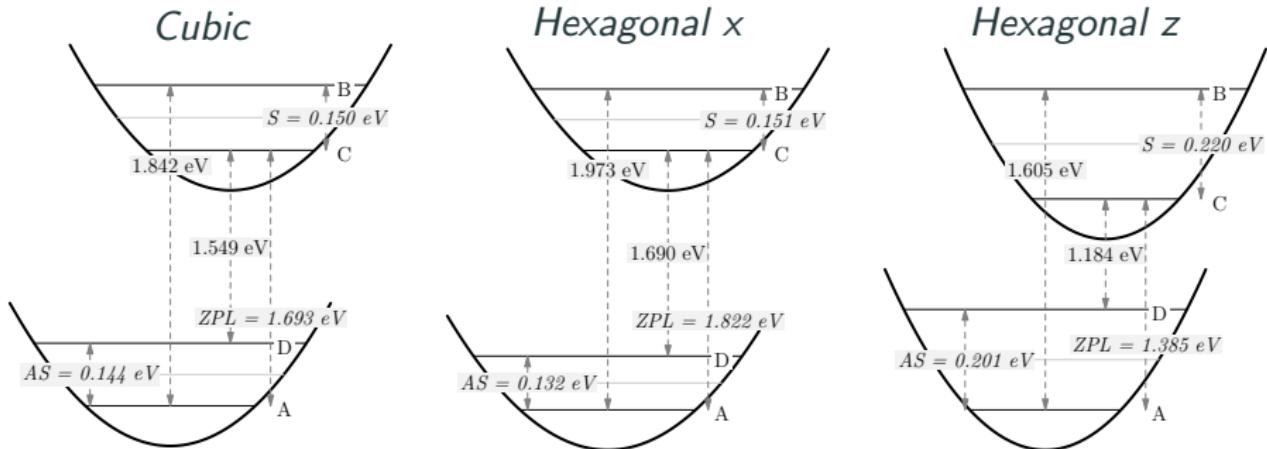
NV⁻: Excited state 3E



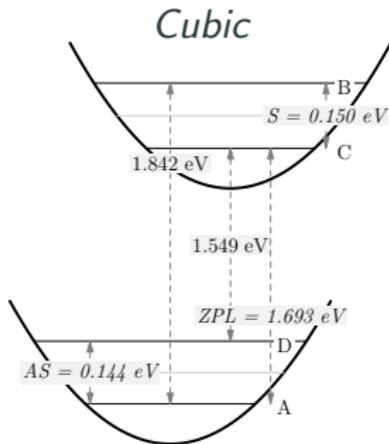
NV⁻: Vibronic scheme (PBE + 128 atomic cell)



NV⁻: Vibronic scheme (PBE + 128 atomic cell)



NV⁻: Vibronic scheme (PBE + 128 atomic cell)



Experimental data	
ZPL	1.945
$^3A_2 \rightarrow ^3E^*$	2.180
S	0.235
$^3E \rightarrow ^3A_2^*$	1.760
AS	0.185

Calculations	
ZPL	1.693
$^3A_2 \rightarrow ^3E^*$	1.842
S	0.150
$^3E \rightarrow ^3A_2^*$	1.549
AS	0.144

Expanding the defect

18 VIIA							
							2 4.0025 He Helium
13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA			
5 10.811 B Boron	6 12.011 C Carbon	7 14.007 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Flourine	10 20.180 Ne Neon		
13 26.982 Al Aluminium	14 28.086 Si Silicon	15 30.974 P Phosphorus	16 32.065 S Sulphur	17 35.453 Cl Chlorine	18 39.948 Ar Argon		
31 69.723 Ga Gallium	32 72.64 Ge Germanium	33 74.922 As Arsenic	34 78.96 Se Selenium	35 79.904 Br Bromine	36 83.8 Kr Krypton		
49 114.82 In Indium	50 118.71 Sn Tin	51 121.76 Sb Antimony	52 127.6 Te Tellurium	53 126.9 I Iodine	54 131.29 Xe Xenon		
81 204.38 Tl Thallium	82 207.2 Pb Lead	83 208.98 Bi Bismuth	84 209 Po Polonium	85 210 At Astatine	86 222 Rn Radon		
113 284 Uut Ununtrium	114 289 Uug Ununquadium	115 288 Uup Ununpentium	116 293 Uuh Ununhexium	117 292 Uus Ununseptium	118 294 Uuo Ununoctium		



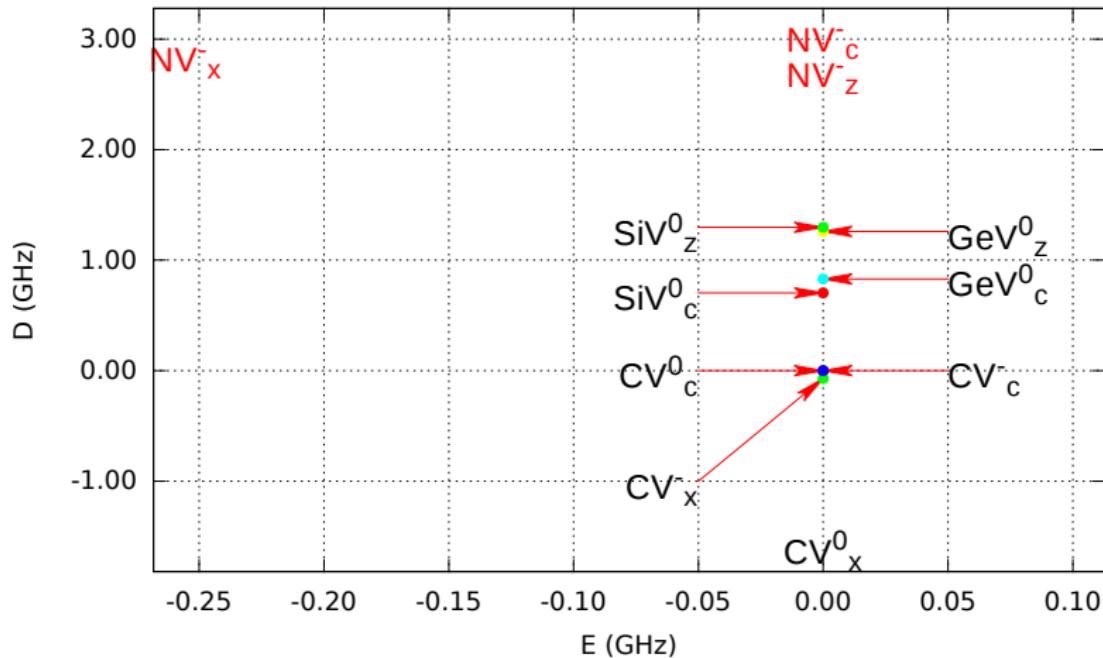
Expanding the defect

14 IVA 15 VA

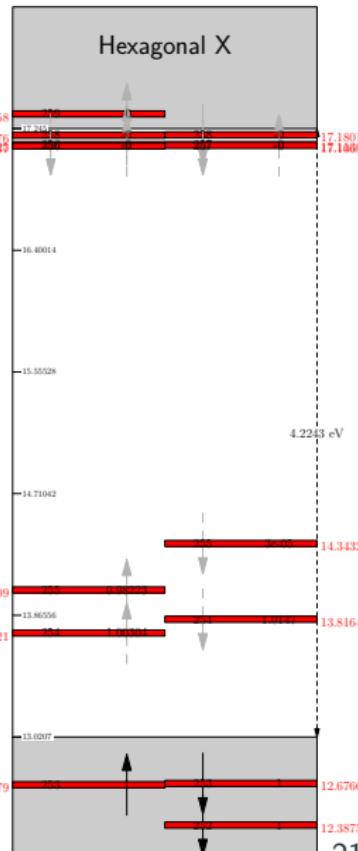
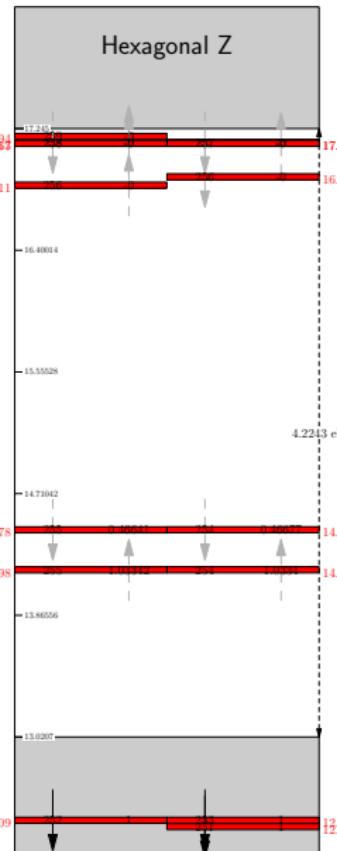
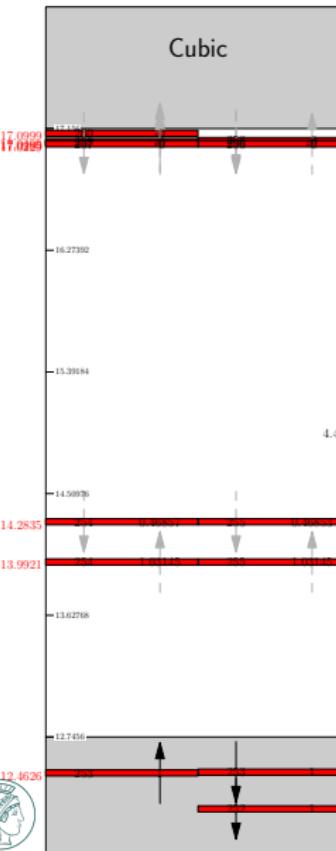
6	12.011	7	14.007
$\text{CV}_{\textcolor{red}{a}}^q$		$\text{NV}_{\textcolor{red}{a}}^q$	
Carbon		Nitrogen	
14	28.086	15	30.974
$\text{SiV}_{\textcolor{red}{a}}^q$		$\text{PV}_{\textcolor{red}{a}}^q$	
Silicon		Phosphorus	
32	72.64		
$\text{GeV}_{\textcolor{red}{a}}^q$		$a = \{c, x, z\}$ $q = \{+, -, 0\}$	
Germanium			



ZFS map



Ground state example: GeV^-



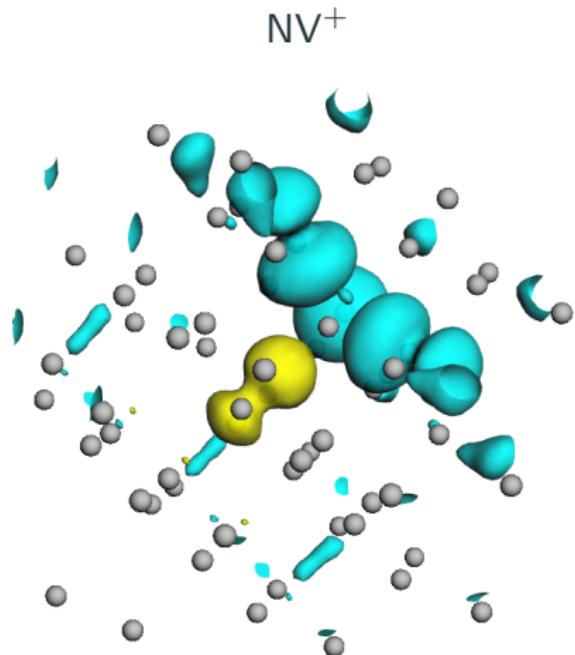
Summary and outlook

Where we are, and where to go next...

- Structural properties
- ZPL calculation.
- ZFS tensor calculation.
- **Beyond the Ground state:**
Using DMRG (*Density Matrix Renormalization Group*) for excited state calculations

Using DMRG for excited state calculations

- XV^q as molecules.
- Localized states as isolated.
- Issues like charge transfer, charge corrections.



Thank you!

