

# 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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Introduction

Hexagonal diamond and defects

Results

Summary and outlook



# Ab initio studies ...

## └ Contents

### Contents

Aim and scope of the work

Introduction

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Results

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**

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# 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.

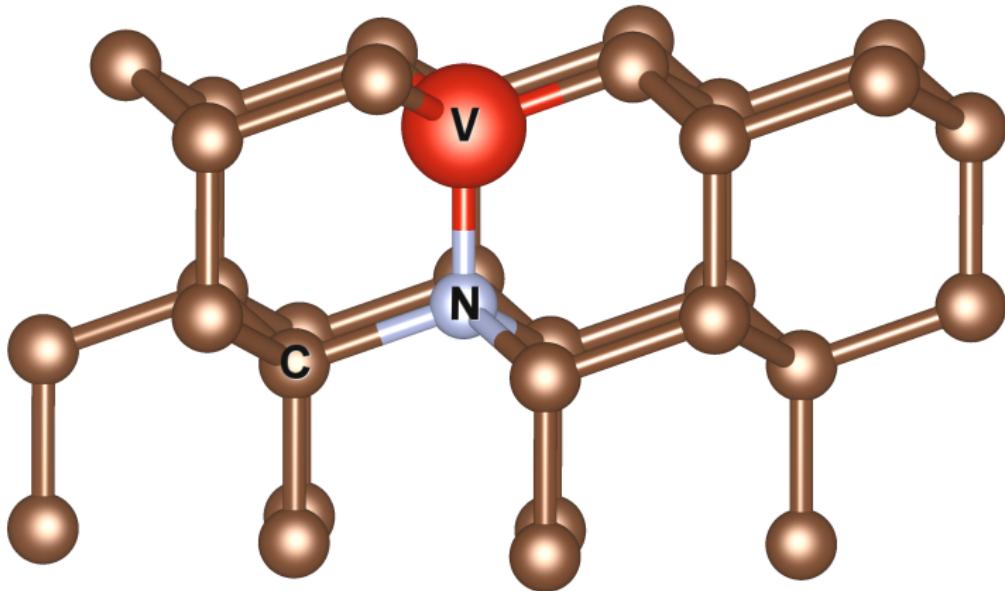
Through this exploration we hope to recover many well-known experimentally verified quantities.

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

# Introduction

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# Nitrogen Vacancy Centre in diamond (NV center)

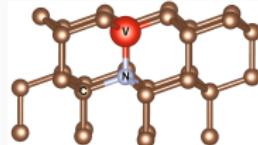


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Ab initio studies ...

└ Introduction

└ Nitrogen Vacancy Centre in diamond (NV center)



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

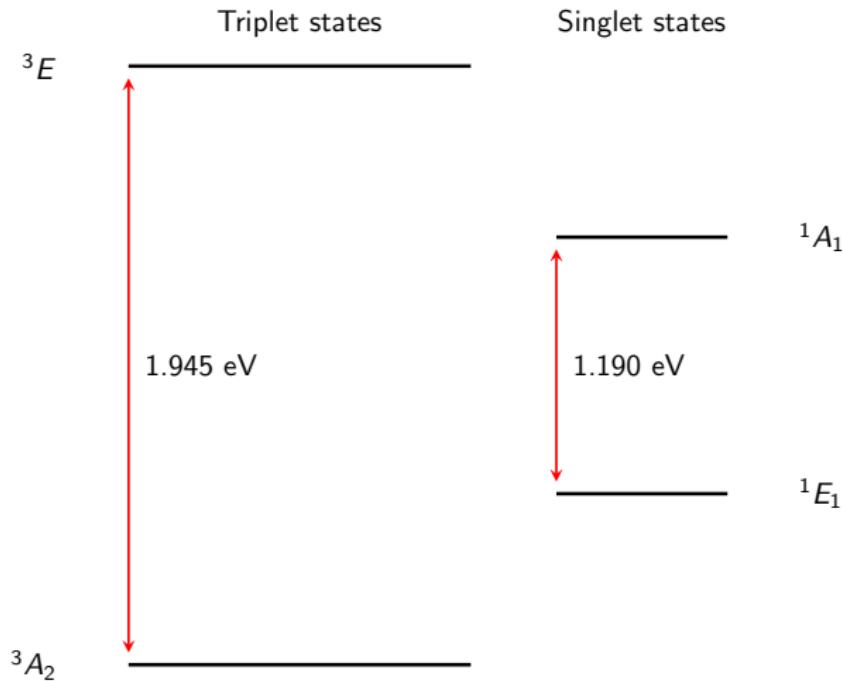
This is the Nitrogen vacancy impurity center in diamond, as most of you may already know. The big red region is a vacant carbon site and next to it lies a nitrogen atom.

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.

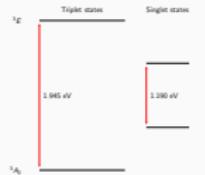
The most notable and studied of the NV centers is the negatively charged one.

# Main level overview: NV<sup>-</sup>



## Ab initio studies ...

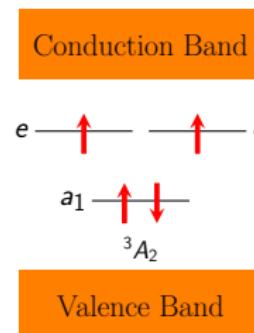
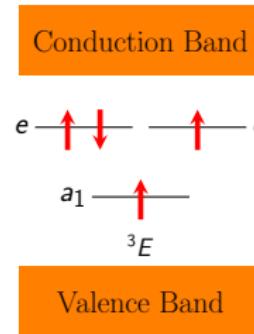
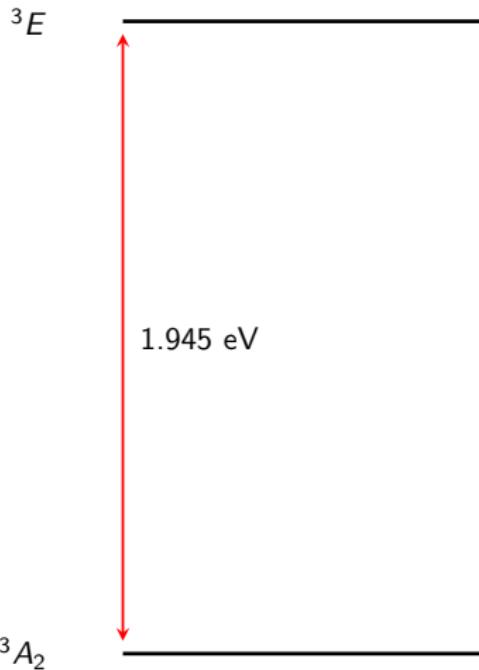
## └ Introduction

└ Main level overview: NV<sup>-</sup>Main level overview: NV<sup>-</sup>

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.

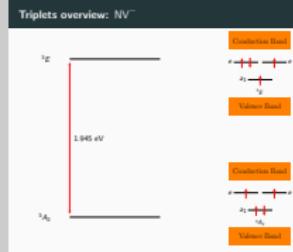
# Triplets overview: NV<sup>-</sup>



Ab initio studies ...

└ Introduction

└ Triplets overview: NV<sup>-</sup>



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.

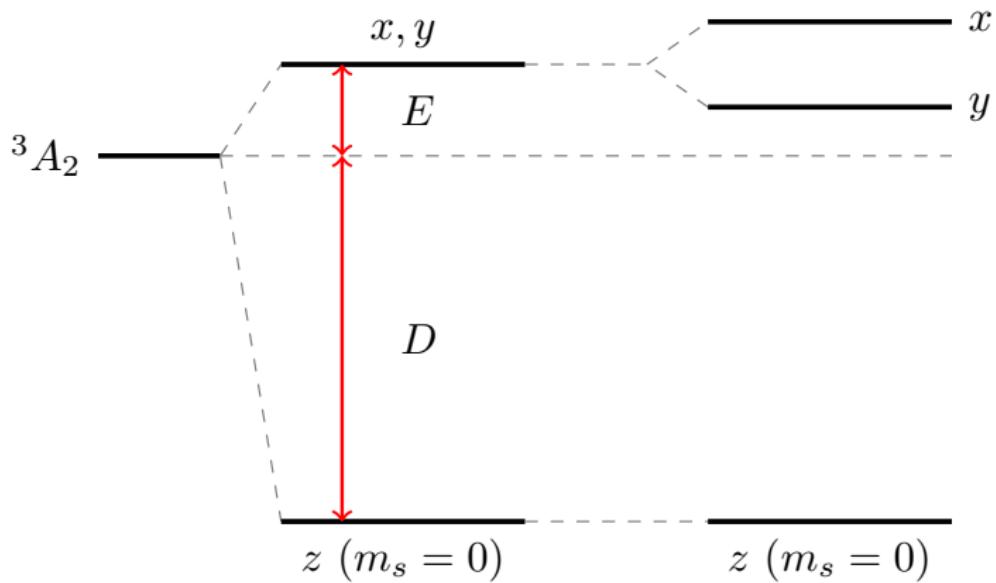
In this picture we can associate to every state with an occupation of the topmost states. From this picture we can see that the total spin is one and the excitation happens through the promotion of one electron in the level  $a_1$  into one of the degenerated  $e$  levels. This without incurring in a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

This we should also find in our calculations.

# Zero Field Splitting (ZFS)

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

Zeeman/strain



REVISE E AND D



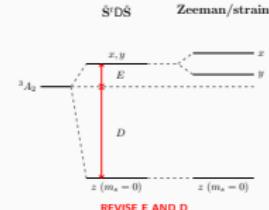
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Ab initio studies . . .

└ Introduction

└ Zero Field Splitting (ZFS)

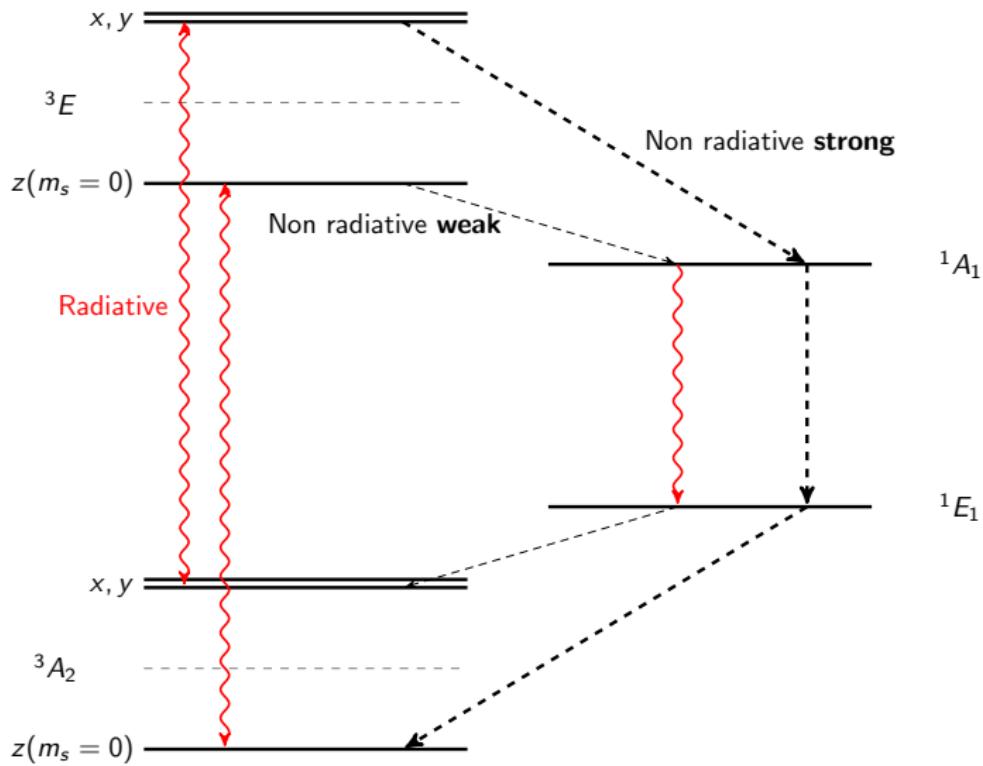


Another important aim of our project is to calculate correctly the zero field splitting of the energy levels.

In this case we are interested in the splitting that arises from the Spin-Spin interaction of the electrons. This splits into up to three levels the triplet state. This splitting is characterised by two parameters,  $E$  and  $D$ .

The splitting also arises through strain of the material and Zeeman splitting.

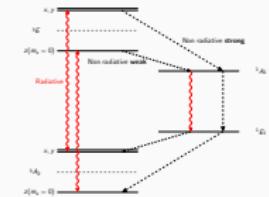
# Transitions overview: NV<sup>-</sup>



Ab initio studies ...

└ Introduction

└ Transitions overview: NV<sup>-</sup>

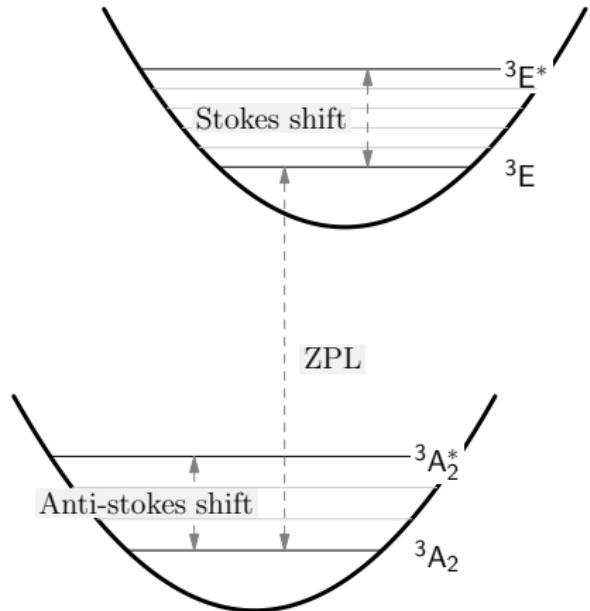
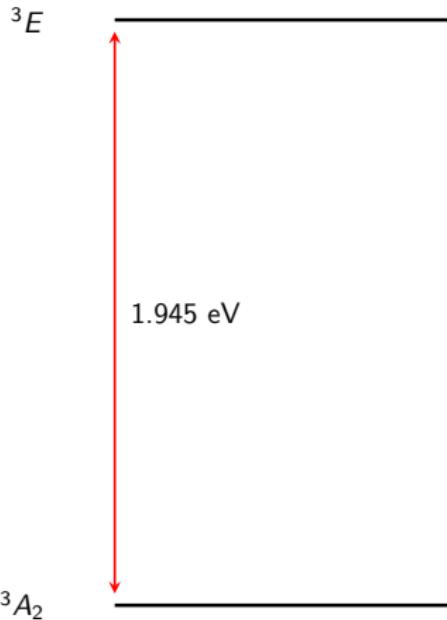


One of the main uses that these levels have in common applications of the NV center is best understood by the following diagram. In it we see the triplets on the left with a splitting in place and the singlet states on the right.

To understand this diagram imagine that the level population of the  $m_s = 0$  in the  ${}^3A_2$  state is much higher than the  $x, y$  split states of the same state. If we radiate with the right frequency of the energy difference between both triplet states, then a non radiative transition brings the system into the singlet state, where a radiative transition happens. In both possible cases, radiation is produced, therefore a detector would take a hold of this radiation.

If the whole population is however in the upper  $x, y$  states, when radiating, since the non radiative transition to the singlet states is strong,

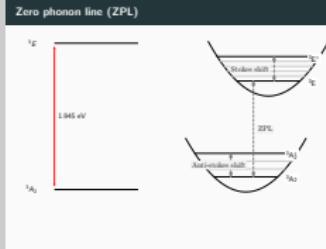
# Zero phonon line (ZPL)



Ab initio studies ...

└ Introduction

└ Zero phonon line (ZPL)



To interpret quantitatively some experiments the previous picture falls short in some regards.

Every electronic state is dependent on the ionic constellation. This gives rise to the so-called vibronic states. For example the ground state has associated with it a given ionic constellation. Through excitation to the upper lying triplet state since the dynamic of the electrons is much faster than the ionic one, the constellation first stays static and then relaxes because the potential landscape changed due to the difference in the electronic density.

This gives rise to two different excited states, which must be considered in order to reproduce experimental data.

A very important quantity in this respect is the so-called zero phonon line, which as its name indicates characterizes the position of the

# Density functional theory (DFT)

*“ $\Psi$  contains too much information”*

*- Popular saying*

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

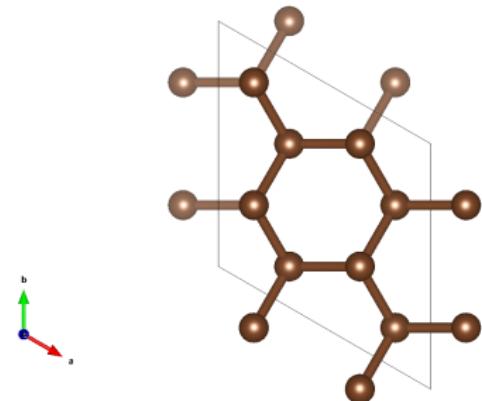
$$E[\rho] = T_s[\rho] + \int V(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}^{\text{exact}}[\rho]$$

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.

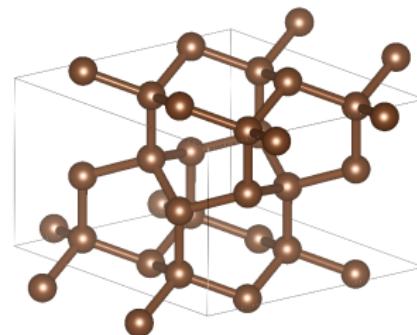
## **Hexagonal diamond and defects**

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# Hexagonal diamond



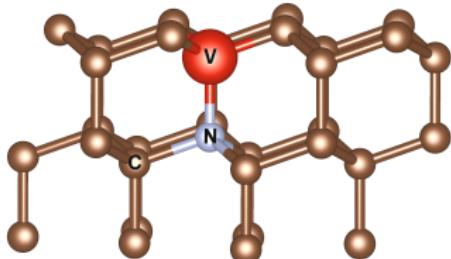
b  
a



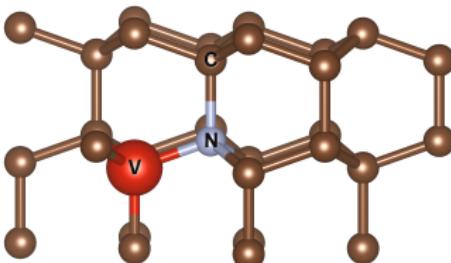
c  
b  
a

# Defected hexagonal diamond

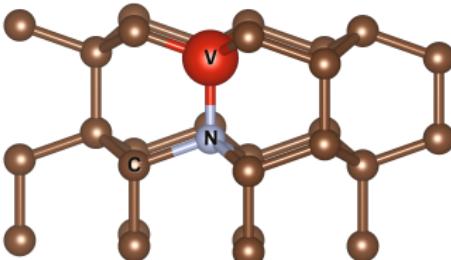
Cubic diamond



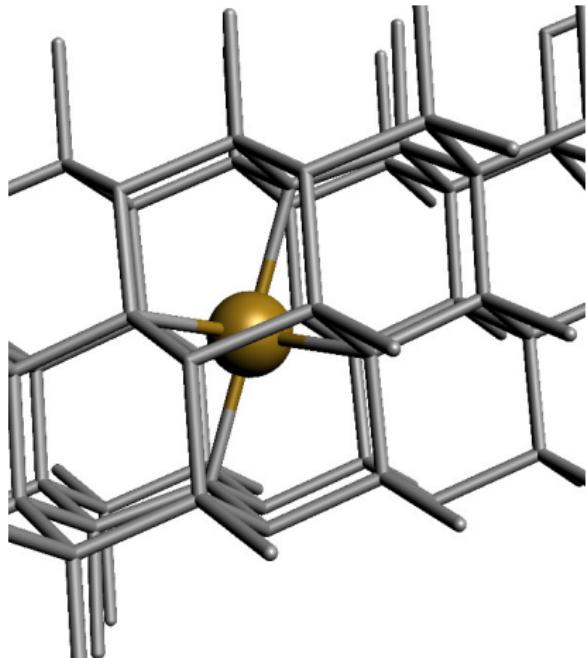
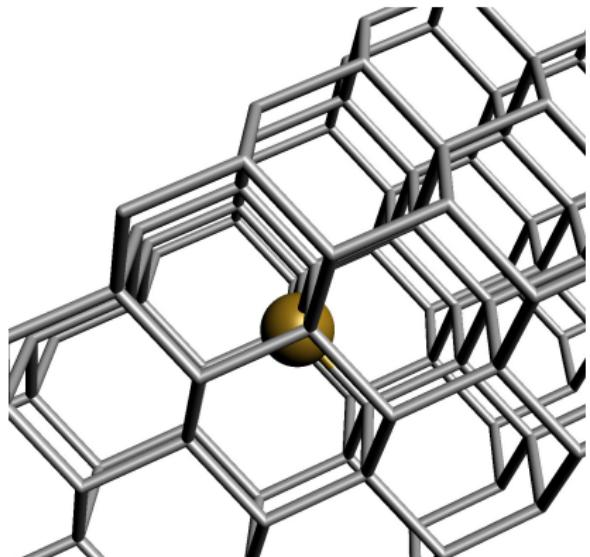
Hexagonal *x*-type



Hexagonal *z*-type



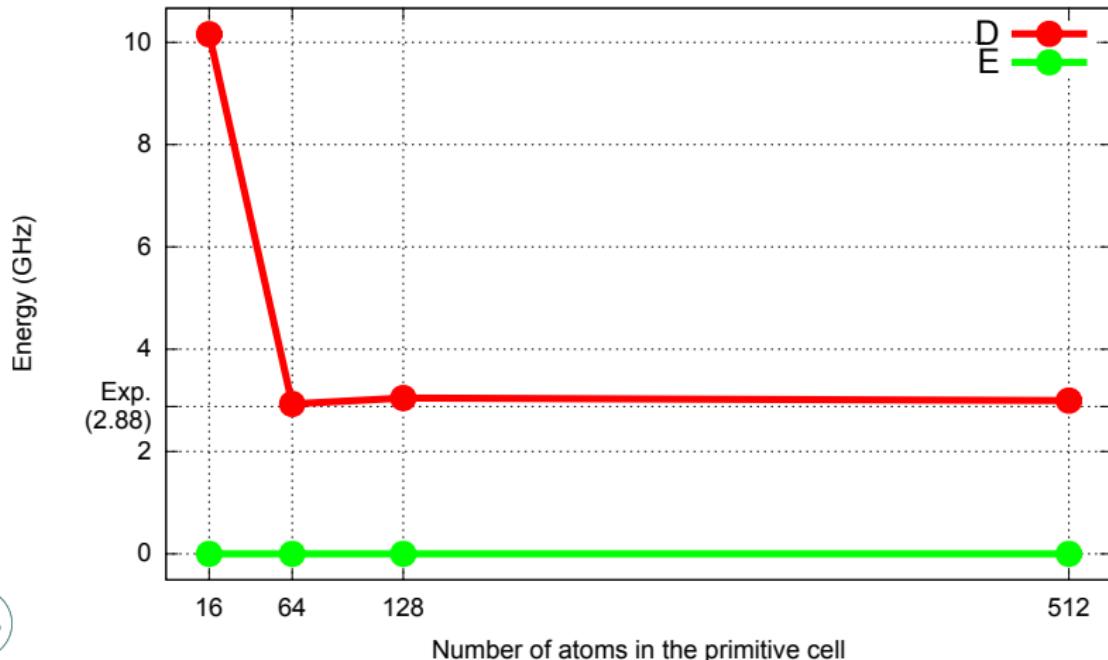
## Split vacancies: SiV<sup>-</sup>



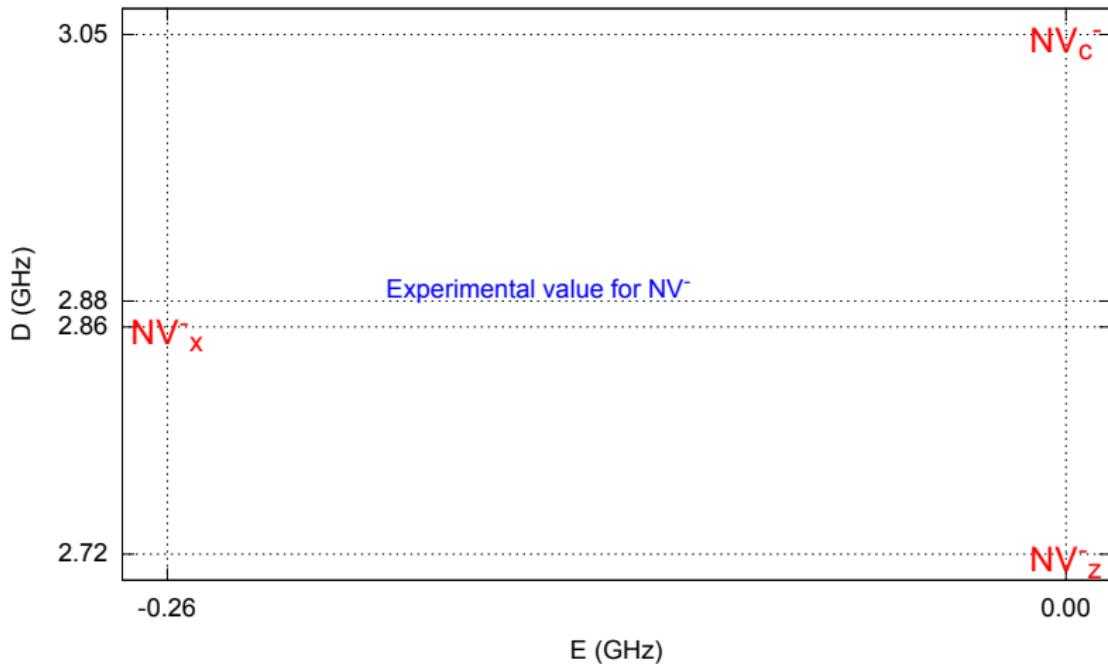
## Results

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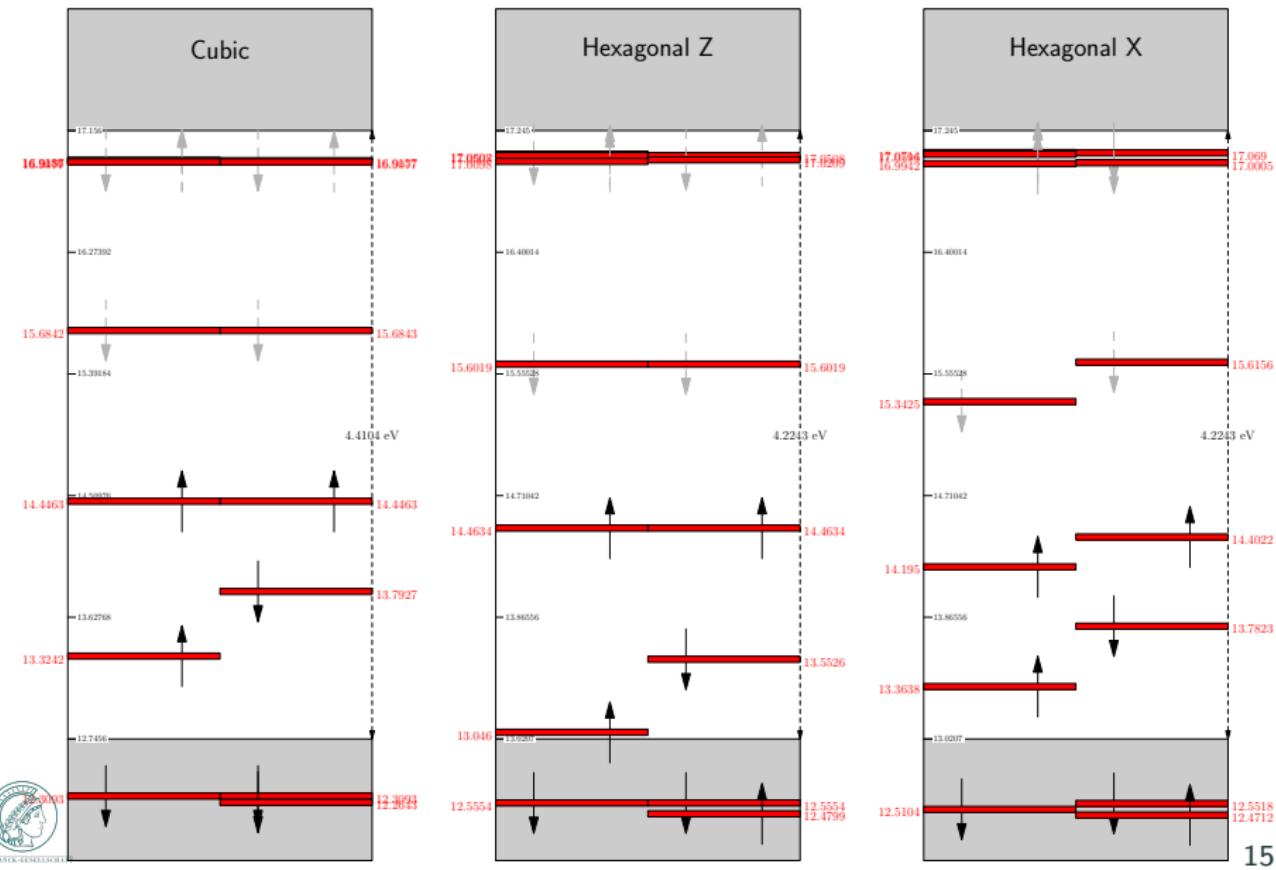
- Cubic diamond, convergence and comparison with the experimental result.



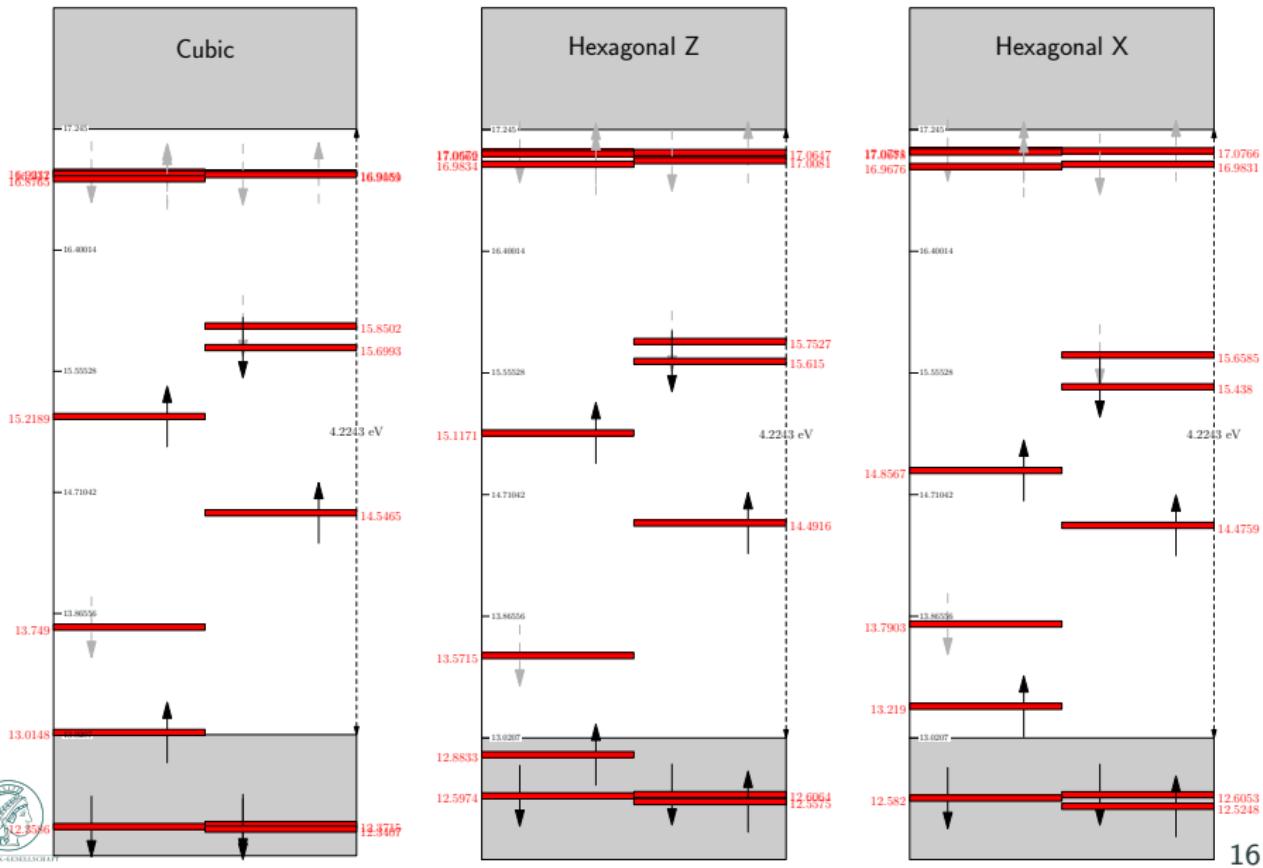
# NV\*: ZFS cubic ( $\text{NV}_c^*$ ), Hexagonal $x, z$ ( $\text{NV}_{x,z}^*$ )



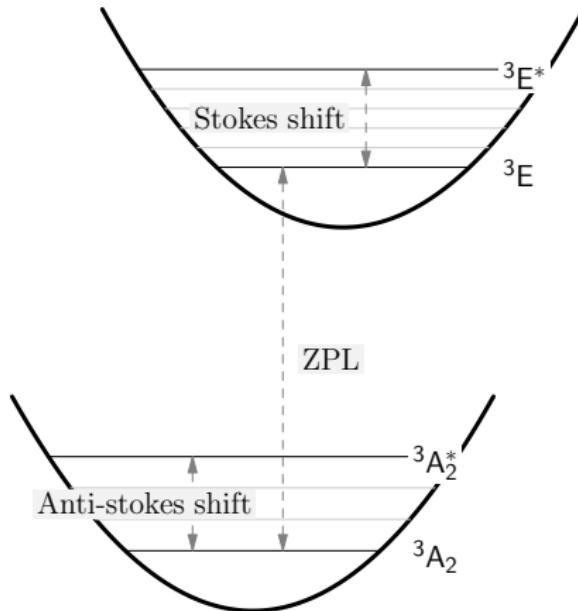
# NV<sup>-</sup>: Ground state $^3A_2$



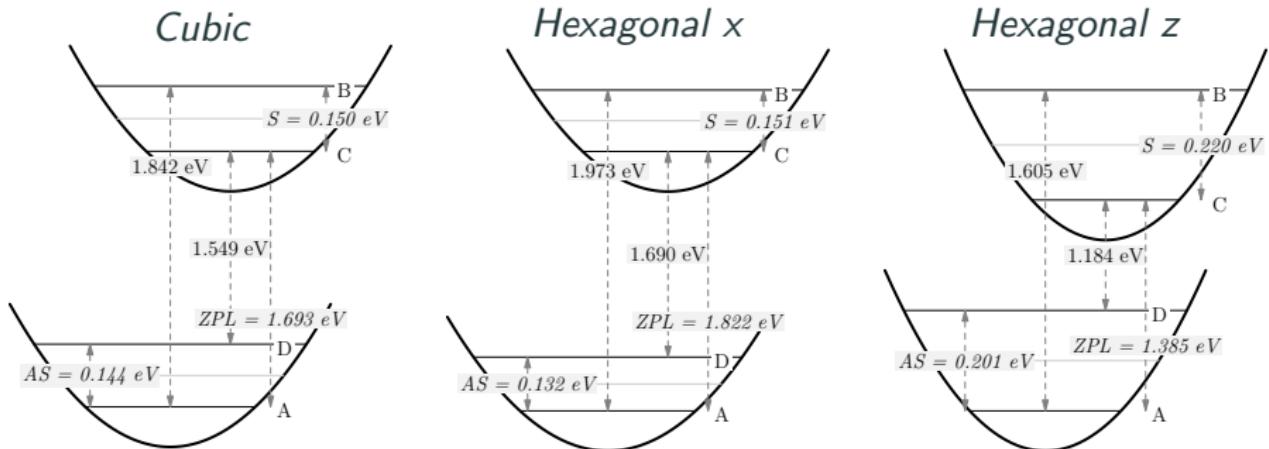
# NV<sup>-</sup>: Excited state $^3E$



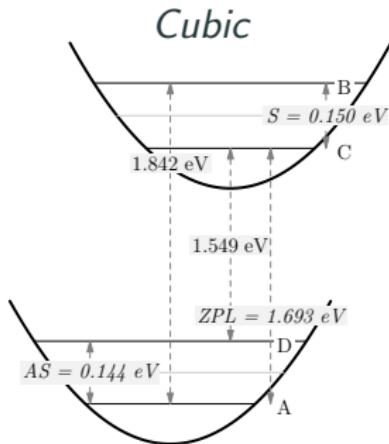
# NV<sup>-</sup>: Vibronic scheme (PBE + 128 atomic cell)



# NV<sup>-</sup>: Vibronic scheme (PBE + 128 atomic cell)



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



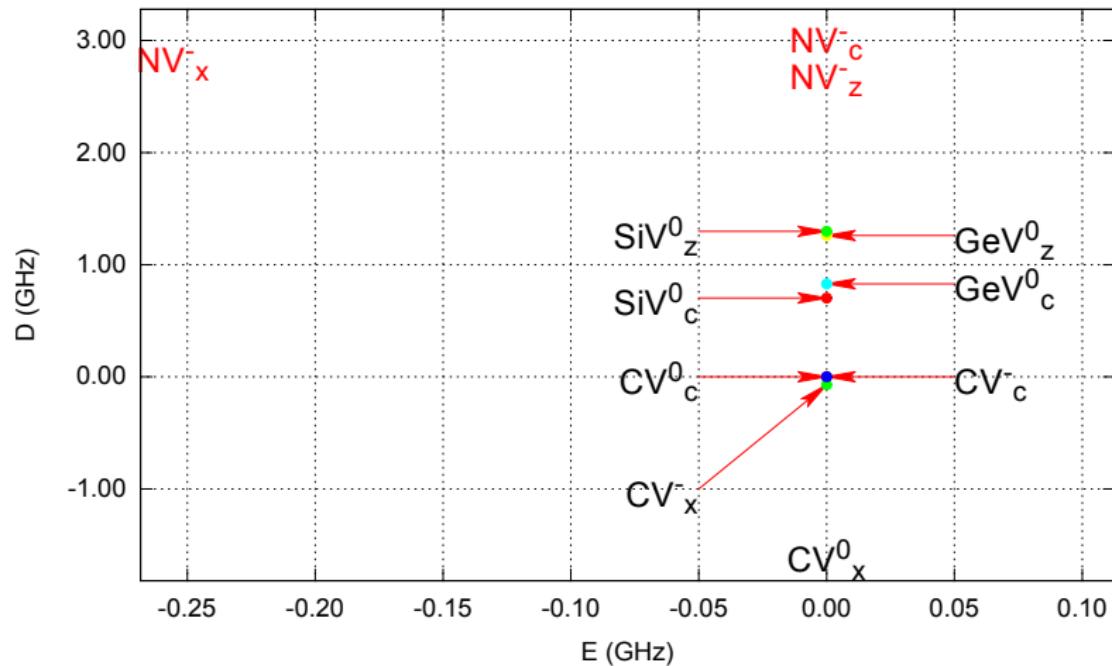
# Expanding the defect

14 IVA      15 VA

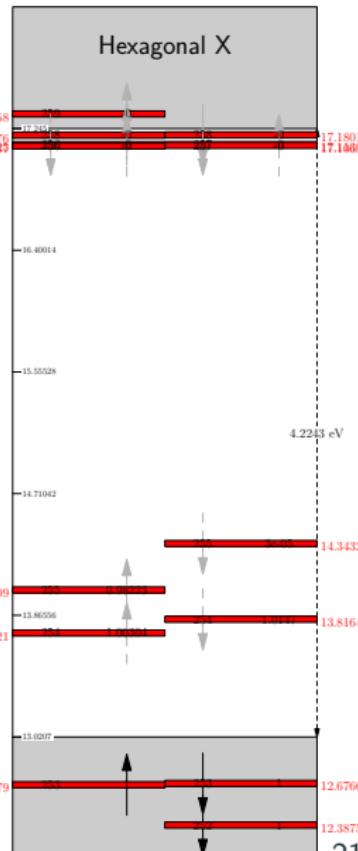
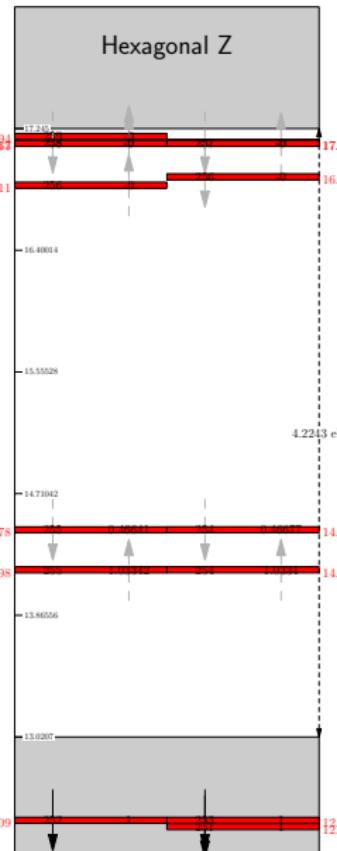
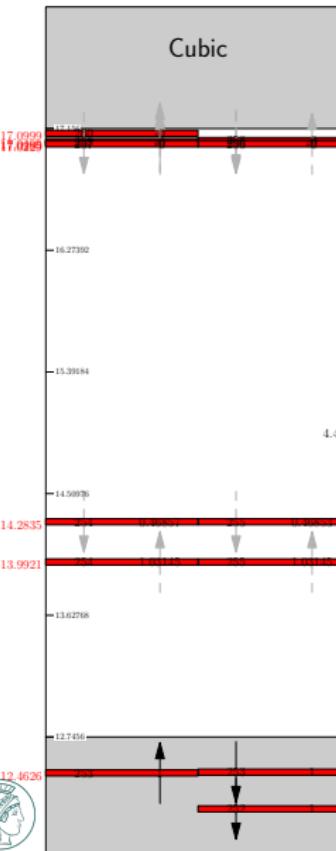
6	12.011	7	14.007
$\text{CV}_{\textcolor{red}{a}}^q$		$\text{NV}_{\textcolor{red}{a}}^q$	
Carbon		Nitrogen	
14	28.086	15	30.974
$\text{SiV}_{\textcolor{red}{a}}^q$		$\text{PV}_{\textcolor{red}{a}}^q$	
Silicon		Phosphorus	
32	72.64		
$\text{GeV}_{\textcolor{red}{a}}^q$		$a = \{c, x, z\}$ $q = \{+, -,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



# ZFS map



## Ground state example: $\text{GeV}^-$



## **Summary and outlook**

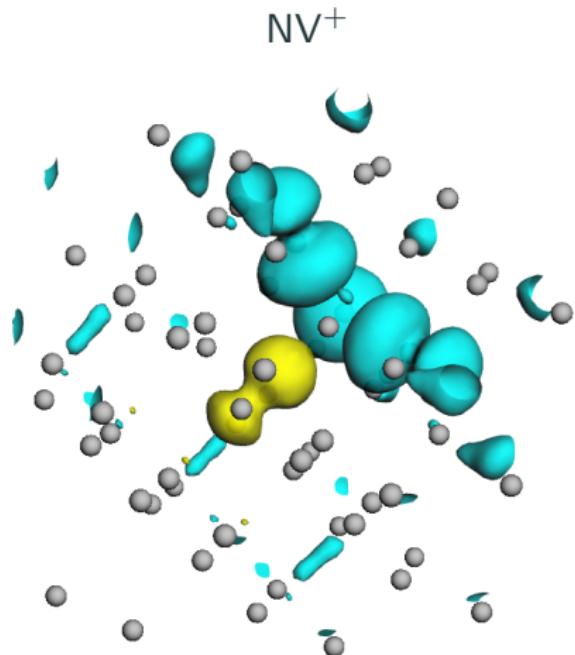
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# Where we are, and where to go next...

- 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!**

