Executive Summary of the Thesis

Study on NV-center Stability in Diamond Nanoparticles for Quantum Information Science Applications

Laurea Magistrale in Nuclear Engineering - Ingegneria Nucleare

Author: Francesco Martinelli

Advisor: Prof. David Dellasega

Co-advisors: Prof. Giulia Galli, Dr. Arpan Kundu

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1. Introduction

In the modern era of scientific and technological advancements, exploring and understanding complex systems have become fundamental to tackle all the most challenging engineering problems. From climate modeling to plasma simulations, from neutronic modeling in fission reactors to interfacial chemical reaction studies, diverse research fields converge on the common need for robust solutions to complex problems. Central to this pursuit is the relentless demand for computational power, which continues to escalate as the intricacy of the systems under investigation deepens. Computational power demands that strain the limits of conventional computing architectures.

Enter the domain of quantum computing, an area that holds immense promise for revolutionizing the landscape of computation-intensive tasks, could be the solution to this need.

In the multifaceted field of quantum computer realization, the most important platforms that have been developed are the superconducting circuits, the trapped-ion technology, the photonic circuits, the quantum annealers and the solid-state platforms.

Within all these possibilities, molecular qubits are extremely promising, thanks to their tunability in the design phase and coupling with the environment. Additionally, some molecular qubits can operate at or near room temperature, potentially reducing hardware complexity and costs.

2. NV-center Embedded in Diamondoids as Molecular Qubits

We have decided to explore the domain of molecular qubits investigating the possibility of embedding an optical-active defect, the NV-center, inside small diamond nanoparticles, to exploit all the advantages that characterize the exploitation of molecular environments.

The nitrogen-vacancy (NV) center in diamonds has rapidly emerged as one of the most promising solid-state systems for quantum information processing and nanoscale quantum sensing. This optically active point defect consists of a substitutional nitrogen atom adjacent to a vacancy in the diamond crystal lattice (in figure 1).
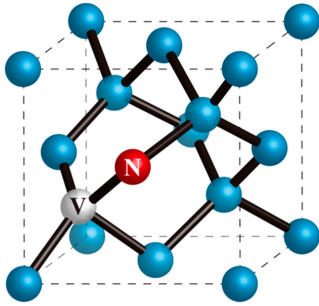
Figure 1: Atomic structure of the NV-center. [3]

In its negatively charged state (NV⁻), it possesses a unique combination of spin and optical properties that make it remarkably suited for quantum technologies.

The appeal of NV⁻ centers for quantum information stems from their optical addressability and spin coherence at room temperature.

The combination of long spin coherence and optical spin control has enabled demonstrations of quantum algorithms at room temperature using one or a few NV⁻ center qubits. [6]

The other crucial component of the system is the hosts of the NV-center.

Diamondoids are a class of nanometer-sized hydrocarbon molecules that have a structure resembling that of diamonds. They are composed of carbon and hydrogen atoms arranged in a three-dimensional, cage-like structure.

(a) $C_{35}H_{36}$
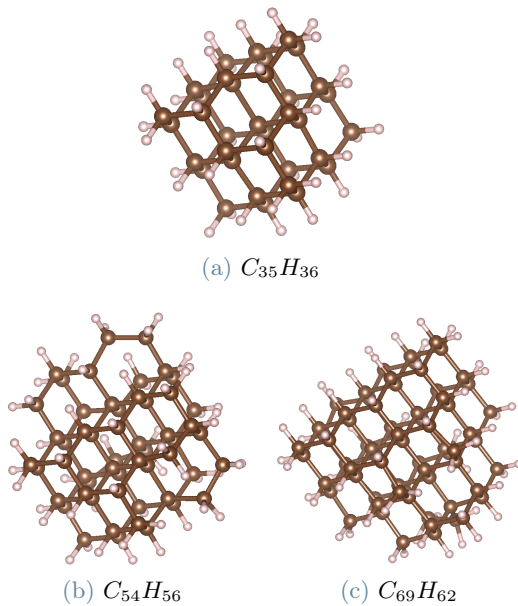

(b) $C_{54}H_{56}$

(c) $C_{69}H_{62}$

Figure 2: Different dimension diamondoids used in this work.

Diamondoids, due to their discrete nature, provide a platform for isolating and manipulating individual qubits.

This molecular confinement introduces a level of isolation that minimizes environmental interactions and could enhance qubit coherence. In addition, previous works have demonstrated the possibility of implanting and manipulating NV centers inside nanodiamonds paving the way to the foundation of this work [5].

3. Theoretical Background: the Density Functional Theory (DFT)

DFT is the powerful computational framework employed in this work and within the quantum chemistry and condensed matter physics communities, it stands as an indispensable tool, offering a robust theoretical foundation for elucidating a wide spectrum of phenomena.

In this work, the DFT is used within the Born-Oppenheimer approximation, which simplifies the quantum mechanical description of the analyzed system by separating the motion of electrons and nuclei.

Among all the possibilities, in this work, we have used the combined approach of plane waves for the valence electronic wavefunctions and pseudopotentials to describe the core electrons, which is a novel approach to study these molecular systems.

The Born-Oppenheimer approximation prevents the electron-phonon interaction from being included in a single-point DFT calculation; however, several types of statistical algorithms can be established to retrieve the phonon effect using DFT single-point calculations.

This avoids the need for computationally costly quantum molecular dynamics simulations while still enabling the computation of the electron-phonon renormalization with a certain level of statistical accuracy.

We have exploited the Harmonic Approximation to evaluate the electron-phonon-renormalized electronic structure of the pressurized molecular crystal, exploring different statistical algorithms. [4]

4. Materials and Methods

In this work, the main feature that we want to recognize in the electronic structure is the presence of localized orbitals inside the vacancy, so it is necessary to define a measurement for this figure of merit.

We explored two different approaches: one is based on the inverse participation ratio (IPR) while the other is based on a selective integral of the wavefunction squared.

$$IPR_i = \int |\Psi_i(\mathbf{r})|^4 dV, \qquad (1)$$

The first approach relies on the comparison between the most localized orbital in the pristine nanostructure and each orbital in the NV-nanostructure: if the IPR of the wavefunction of the NV-nanostructure is higher than double the IPR of the pristine's most localized wavefunction, the NV one's is considered localized.

$$loc_i = \int_{V \subseteq V_{sphere}} |\Psi_i(\mathbf{r})|^2 dV, \qquad (2)$$

The second approach is local and relies on the calculation of the integral over the sphere or radius 1.5Å (C-C bond length) centered in the vacancy: if the orbital is more than 50% localized inside the sphere, it is considered localized.

The reason why both of these methods were considered is that is difficult to define a measure for the localization in a molecular system, that is itself localized.

However, except where it is clearly mentioned, in this work the second method was chosen as the reference one since it allows to discriminate the position of the localization, so it is possible to understand where the orbital is localized, not just if it is localized.

5. NV-diamondoids Electronic Structure

We have analyzed three different diamondoids: $C_{35}H_{36}$, with a cage dimension of $\sim$ 7 Å; $C_{54}H_{56}$, with a cage dimension of $\sim$ 8 Å; $C_{69}H_{62}$, with a cage dimension of $\sim$ 8 Å.

Once the NV center has been implanted, we have evaluated the electronic structure (in figure 3) and we have found that all of them are characterized by a negative electron affinity.

Moreover, we have been able to observe the evidence of the quantum confinement effect, which increases the gap as the nanoparticle dimension decreases, and the distortion-related delocalization effect in the two bigger clusters.
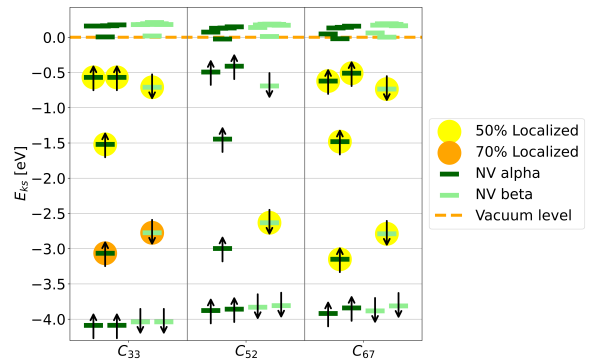

Figure 3: Electronic structures comparison between $C_{33}H_{36}NV^-$, $C_{52}H_{56}NV^-$ and $C_{67}H_{62}NV^-$.

These results show that the small nanoparticles with a number of carbon atoms less than 87, which complete the second carbon shell, cannot be used for the purpose of quantum information application, since it is impossible to excite an electron localized in the NV-center, without expelling the electron from the nanodiamond. However, the presence of a well-defined NV-center electronic structure inside the gap motivated us to search for some solution to engineer the nanoparticles with the aim of making them suitable for qubit use.

6. Surface Functionalization

A possible idea to improve the electronic properties of the NV-nanodiamonds is to functionalize the nanoparticles' surface with electron-withdrawing functional groups or atoms.

As a general chemical idea, the electron-withdrawing group draws electron density toward itself, creating more space to accommodate the additional NV-electron, which is stabilized since the Coulomb repulsion decreases.

Among the terminations that we have explored (Fluorine, Hydroxyl, Thiol, and Carbonyl) only

the F-terminated nanoparticle revealed their promise for applications.

In fact, it can be seen that, despite the stabilizing behavior shown by all the terminations, only the Fluorine is able to reconstruct the complete NV-center electronic structure, with both the empty defect levels within the gap.
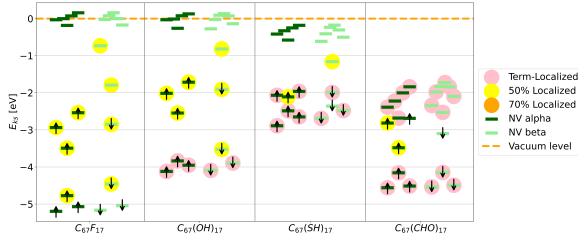

Figure 4: Electronic structure comparison between the structures terminated with 17 functional groups.

The analysis of the radial potential in each nanoparticle shows that the reduced Coulomb repulsion stabilizes the unoccupied levels of the nanodiamonds with different terminations, as evident from the radial Coulomb potential, which is highest for the H-terminated nanodiamond.
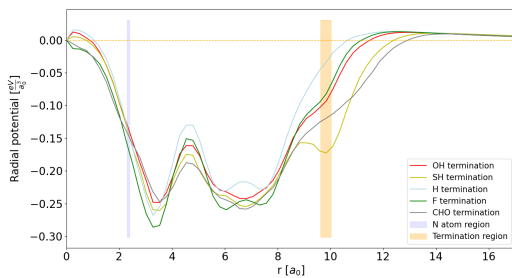

Figure 5: Radial potential comparison between each termination, with a focus on the NV region.

This evidence underlines the importance of the chemical concept of withdrawing/donating functional group, since the stabilization process occurs due to the modification of the Coulomb potential, without the necessity to include electron exchange and correlation contributions. During the exploration of the different terminations we have found that only the F-termination does not damage the defect levels within the gap. In fact, all the other terminations localize the spin density slightly outside the NV or

delocalize some of the NV-localized levels, which is undesirable for applications.

7. Pressure and Temperature Effect on Diamondoids Molecular Crystals [1]

Lastly, we have decided to study a diamondoid-based molecular crystal because it approaches the idea of building a proper quantum hardware, in which qubits are not isolated, but they can be entangled, and, in general, interact with each other.

In such a system it is possible to explore the effect of macroscopic variables such as temperature and pressure. In fact, different works showed the effectiveness of pressure in controlling the electronic structure of the crystals on which it acts, and in particular on the diamond electronic structure [1].

On the other side of the picture, since the population of the different phonon modes can have a significant impact on our system's electronic structure, is crucial to study the effect of temperature, in order to establish the reliability of the qubit at room temperature. [2] We have analyzed both the $C_{67}H_{62}NV^-$ and $C_{67}H_{45}F_{17}NV^-$ when they form a BCC no-point symmetric molecular crystal, but only the latter has shown promising characteristics in the quantum information domain.
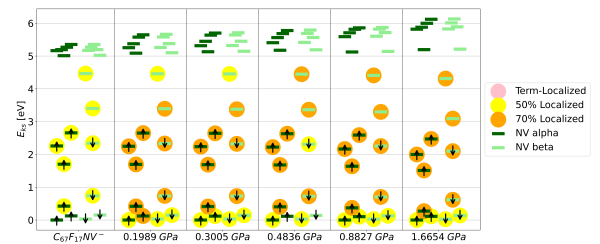

Figure 6: Electronic structures comparison for the $C_{67}H_{45}F_{17}NV^-$ BCC molecular crystal under different pressures.

In the $C_{67}H_{45}F_{17}NV^-$ electronic structures NV-levels localization increases, valence band localizes, and conduction band energy increases

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[1]This chapter has been developed within the context of the Honours Programme "Scientific Research in Industrial Engineering".

as well, with Conduction Band Minimum (CBM) stationary.

The pressure effects are favorable since the NV electronic structure is still complete but improved in localization. Moreover, we note that here the separation between the highest in energy empty defect orbital and the CBM is of 0.9 eV, which is positive for practical quantum protocol implementation since the risk of exciting one of the NV-electrons to a delocalized level is reduced.

The localization effect is related to the enhanced Coulomb repulsion between the electronic cloud when the distance between consecutive nanoparticles decreases.

On the other hand, the conduction band energy increase is related to the quantum confinement effect since, at a certain pressure, the empty orbitals collapse in between the nanoparticles, and the confinement length of the electron in those orbitals decreases as the pressure increases. The CBM is stationary because it remains always localized on the nanoparticle during the pressurization.

This behavior can be compared with the particle-in-a-box model, which has been fundamental to obtain a phenomenological interpretation of the results.

After having studied the effect of the pressure on the molecular crystal, we have refined the description of our system including the electron-phonon interaction in the high-pressure molecular crystal.

First of all, we have carried out calculations at $T = 0\ K$ to obtain precious insight on the low-energy phonons effect.

Within the acquired accuracy, the magnitude of the electron-phonon renormalization does not change the electronic structure of the molecular crystal significantly (in figure 7) and confirms the system's promise for quantum information applications.

In particular, we can notice that, even if the gap is reduced, the defect levels are almost unaffected by the phonon coupling.

Then, we have assessed the impact of the phonons on the molecular crystal electronic structure at room temperature ($T = 300\ K$).

We can notice in figure 8 that the electronic structure is preserved, and the magnitude of the electron-phonon renormalization does not

change as the temperature increases, underlining the insensitivity of the electronic structure of this system to temperature variation, which is crucial for a room-temperature qubit system.
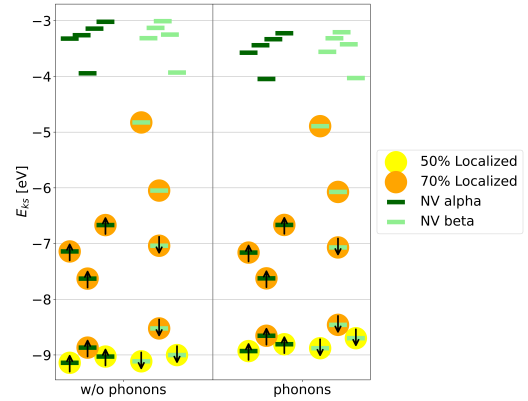

Figure 7: Electronic structures of the $C_{67}H_{45}F_{17}NV^-$ molecular crystal at 1.665 GPa when the electron-phonon interaction is considered.
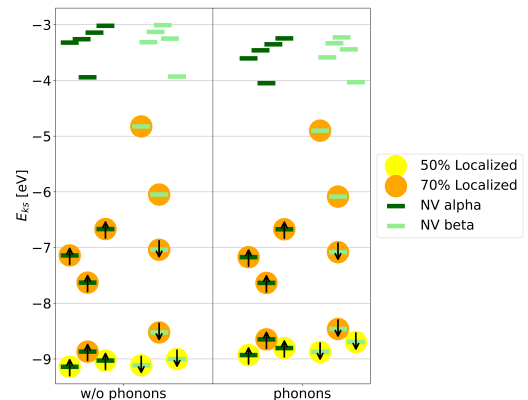

Figure 8: Electronic structures with the electron-phonon renormalization of the $C_{67}H_{45}F_{17}NV^-$ molecular crystal at 1.665 GPa and 300 K.

8. Conclusions and Future Research

During the course of this theoretical and computational study, developed within the Density Functional Theory framework, we have unveiled several noteworthy findings.

We have established that isolated H-terminated diamondoids, in which the NV-center is embedded, lack the presence of localized empty states below the vacuum level.

Then, we have demonstrated that terminations involving hydroxyl (OH), thiol (SH), or carbonyl (CHO) groups offer the advantage of stabilizing nanodiamonds, guaranteeing a positive electronic affinity.

However, only the fluorine termination has demonstrated the capability to effectuate a complete reconstruction of the NV electronic structure. Finally, we have analyzed the effects of pressure on diamondoid molecular crystals and we have also included the electron-phonon interaction, which allows also to account for the temperature effect on the electronic structure.

It emerged that pressure exerts a favorable influence from the perspective of practical applications since the increase in the gap guarantees a more spacious accommodation for the NV-levels.

Furthermore, the gap is only slightly reduced by the electron-phonon renormalization, which is not harmful to the applications, even at room temperature.

In light of this, the implications arising from these numerical findings hold promising significance within the domain of quantum information science, giving a direction to follow for eventual experimental realizations.

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