Hybrid Approach for Calculating Strain due to Nitrogen-Vacancy Centers in Diamond with Coupling to Electronic Structure

Statement of the problem

The objective of this proposal is to calculate lattice distortions and strain arising from Nitrogen-Vacancy (NV) centers in diamond (referred to as NVD) and their relations to electronic structure, using an unprecedented hybrid approach. Density functional theory (DFT) will be used to calculate ionic positions and the potential function, as well as electronic density in the vicinity of NV centers in nanoscale diamond. The multiscale Green function (MSGF) method, developed at NIST Boulder, will be used to relate short range lattice distortions to long range strain fields. Tight-binding methods will be used to further clarify electronic wavefunctions and their coupling to ionic displacements. Despite its 50-year history and potential applicability spanning quantum computation, metrology, and advanced imaging[1,2], many theoretical questions still remain about electronic properties in NVD[3]. The urgency of developing a full scale quantum computer has grown rapidly, with multiple groups recently reporting quantum supremacy, thus amplifying the drive to clarify properties of NVD qubits and how they are affected. Stain is inherent in NVD since translational symmetry is broken, and is more pronounced in nanoscale NVD, affecting many electronic properties with implications for qubit states and manipulations. For its applications to be fully realized, particularly as qubits, the understanding of strain and its effects in NVD must be advanced greatly. This proposed work combines several theoretical tools into a hybrid approach for investigating lattice distortions, strain, and electronic structure in NVD together, resulting in detailed short range electronic properties with clear connections to both short and long range lattice effects in large crystallites. Implications for qubit operation, such as preparation and readout, will be investigated qualitatively.

Background and relevance to previous work

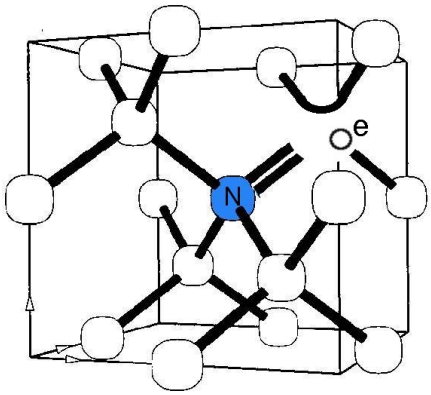

Figure 1: Nitrogen-Vacancy (NV^-) defect in diamond. [From Wikipedia Commons.]

A Nitrogen-Vacancy center in diamond consists of a substitutional Nitrogen atom with a vacancy as one nearest neighbor[1,3] (see Fig. 1), oriented along one of four equivalent crystallographic axes[4]. Nitrogen atoms can take interstitial positions, and vacancies can be further away, but those configurations are energetically unfavorable[5–7]. The relatively stable form of a single nitrogen paired with a vacancy is often created by irradiation and annealing[8]. The NV center typically accepts an extra electron to form a negatively charged state (NV^-), though a neutral state (NV^0) is also possible, guided by optical irradiation[1]. The NV^- state is the most investigated and shows the most promise for real applications. The history of NVD dates back several decades[9], but the detection[10] and highly controlled fabrication[11] of single NV^- centers in diamond have opened several doors to novel applications. Arguably the most notable and pressing application for advancing science and national security is the use of NV^- centers as qubits[12,13], made possible by single photon generation[14] and optical preparation and readout of the center's electronic spin[15]. NVD qubits have been studied at room and cryogenic temperatures, with many demonstrations relevant for quantum computing and information processing[16–19]. Other applications generally fall under metrology, including: nanoscale magnometry, electrometry, and others[1,2].

Lattice distortions accompany each NV^- center, the nearby nitrogen and carbon ions displaced from

crystalline positions, which affect electron hopping energies as well as interactions between electronic and nuclear spins. These parameters dictate electronic wavefunctions and spin states of NV centers, which are crucial to understand and control for successful qubit operations. Electronic properties must be clearly described alongside lattice distortions and strain for NV^- centers to be applicable as room temperature qubits in full scale quantum computers[3], and for other uses, particularly because of the increased strain in nanoscale NVD[1,20]. Previous works have attempted to calculate electronic levels and spin structure for NVD in the presence of strain and other effects[21], but they have not led to fully detailed descriptions[3]. Prior results are also typically limited to short range, often due to using DFT alone, for which computational costs grow rapidly with system size. In other cases, strain had been included phenomenologically as an external factor without lattice distortions due to the NV center. Historically, a perfect lattice was assumed and changes due to the defect were calculated with Slater-Koster or Hartree-Fock methods[22–24]. For real applications of NVD, like quantum computing, it is thus imperative to establish reliable calculations of lattice distortions and electronic details of NV^- centers, with great accuracy and the ability to connect microscopic and macroscopic lattice effects. This is the goal of the work proposed herein.

General methodology

The starting point for this work is modeling NVD within the framework of DFT, which has been widely used for many electronic properties[3,25,26]. The model configuration will be the stable and applicable case of a substitutional Nitrogen atom with a nearest neighbor Vacancy[7]. The primary state of interest is NV^- but, rather than being assumed, specifics like the charge state will be revealed by calculation. A DFT approach built upon Kohn-Sham will be implemented to establish the ground state electronic density as well as ionic positions and elastic constants, using existing VASP software[27]. A generalized gradient approximation, the Perdew-Burke-Ernzerhof (PBE) functional, will be used[28], which is known to produce realistic results and is capable of describing spin-polarized electron systems[3,26]. This is particularly important for NVD

since electron spin-spin and spin-orbit interactions are significant[3]. Spin interactions will be included by appending necessary contributions to the PBE functional. The sample will be modeled as a nanoscale crystallite, consisting of a cubic supercell with ∼100 atoms and the NV center located near the middle.

To investigate the connection between local strain and electronic properties, displacements of lattice ions established by DFT will be utilized. Those ionic (discrete) displacements are related to bulk (continuum) strain. The multiscale Green Function (MSGF) method will be applied to specify the relation between discrete short range lattice displacements, the corresponding continuous displacement field, and the continuous long range strain field. The MSGF, developed at NIST Boulder, is an extension of the lattice static Green function, with a strong history including successful application to point defects like vacancies and connections to molecular dynamics[29–34]. While electronic Green functions are commonly used with DFT, the use of lattice Green functions, MSGF, is a new aspect here which seamlessly connects short and long ranges, effectively extending the simulation to model much larger crystallites. Bridging DFT and MSGF is a new concept with promising applicability; it will be established analogously to methods used in connecting to molecular dynamics[34] and AI-based multiscale modeling[35].

Very briefly, the utility of MSGF originates from the expression for lattice displacement at the n^{th} site, $\vec{u}(\vec{r}_n)$, in terms of Kanzaki forces, $\vec{F}^*(\vec{r}_n)$, shown in Eq. (1). The Green function $\mathbf{G}$ is for a perfect lattice, and changes due to defects enter only via $\vec{F}^*$. The MSGF uses a quasi-harmonic approximation in which any anharmonic effects are captured by Kanzaki forces.

$$\vec{u}(\vec{r}_n) = \sum_{n'} \mathbf{G}(\vec{r}_n, \vec{r}_{n'}) \cdot \vec{F}^*(\vec{r}_{n'}) \tag{1}$$

The discrete GF $\mathbf{G}(\vec{r}_n, \vec{r}_{n'})$ is used for points near the defect, while its asymptotic limit, the continuum-model GF $\mathbf{G}_c(\vec{r}, \vec{r}\,')$, is used for points further away, bridging short and long range. This method is computationally inexpensive and allows for the accuracy of DFT, normally limited to small systems, to

be extrapolated toward the bulk limit. The bulk system will be simulated by imposing cyclic boundary conditions on the supercell used in DFT. NIST has special expertise on the MSGF method and some software will be available for this work; additional custom computer code will be built to expand and adapt existing software as necessary, using C++.

DFT will then use the results from MSGF to classify distorted wavefunctions according to associated strain fields. This will be complimented by the analytical formulation and numerical evaluation of tight-binding integrals (molecular orbital overlaps and hoppings) to clarify the distortions of electronic wavefunctions and energy levels due to ionic displacements. Since this step lies outside the scope of available DFT software, custom computer code will be built in C++, taking results from DFT software as inputs and generating outputs like distorted wavefunctions, energy levels, and spin structure. An approach using the linear combination of atomic orbitals technique has been previously demonstrated alongside calculations from DFT[26]; here that line of thought is taken further, utilizing DFT for initial accuracy then an orbital-based method for efficient and detailed calculations with lattice distortions included. Any qualitative implications for NVD states as qubits will be explored at this stage, including analysis of the optical preparation and readout process with distorted wavefunctions.

The above three-step approach, combining DFT with MSGF and tight-binding methods, is unprecedented and will greatly contribute to the theoretical understanding of strain and electronic structure in NVD while guiding realistic applications of NVD in quantum computation and metrology.

The main assumptions of the approach are:

- The energy functional in DFT depends on local electron density, $\rho(\vec{r})$, and its gradient, $\nabla\rho(\vec{r})$.
- The (quasi-) harmonic approximation for lattice potential energy in MSGF captures key effects.
- An atomic state basis generates accurate, spin-resolved tight-binding parameters.

The following is a tentative timeline for this work:

Months	*Goals*
1–6	Use DFT software to calculate NVD ground state properties
1–6	Extract important features: electron density, ionic positions, lattice potential function
4–12	Connect DFT to MSGF for the lattice, relating short & long range
10–16	Implement MSGF lattice methods; build respective computer code
12–20	Employ tight-binding methods for electronic details; analytic work and numerical code
14–20	Investigate implications for NVD qubits
16–24	Build visualization code; unify all parts of code into a cohesive package

New or unusual methods

The methodology described above consists of three main steps that separately have been successfully applied in many solid state systems. In particular, many variants of DFT have been applied in the context of NVD, exploring various phenomena with differing levels of accuracy. Slater and Koster's linear combination of atomic orbitals (LCAO) and consequential tight-binding techniques have also been applied to explore the electronic properties of NVD in some detail. The MSGF has been used to explore lattice effects in many solid state systems, but it has never been used in tandem with DFT.

Completely new in this proposed work is the hybrid approach from applying these powerful techniques together, with the promise of elucidating the connection between strain and electronic structure of NVD in great detail, with lattice displacements and strain described at short and long range from the NV center.

The great short range accuracy of DFT will be used as the first step, characterizing the electronic and spin structure, and providing the elastic constants and potential function for lattice ions. Next, the MSGF will be applied for lattice details and strain in a systematic way, building a connection to DFT in similarity

to the general technique used in connecting MSGF to molecular dynamics[34]. This connection of MSGF to DFT is unprecedented and will contribute to the state of the art in modeling defect systems like NVD. Lastly, parameters from DFT and MSGF will be used as inputs for the overlap and hopping integrals of the tight-binding method, with displaced ions near the NV center connected to long range strain, resulting in distorted wavefunctions and implications for qubit applications.

This pioneering three-tiered hybrid approach will produce incredibly detailed results relating strain and electronic structure in NVD using DFT and tight-binding methods, and lattice effects incorporated with MSGF building on the short range accuracy of DFT.

Expected results, significance, and application

This proposed work will employ DFT software to calculate electronic structure and lattice distortions in the vicinity of the NV center in diamond. Subsequently, custom computer code will be built for further calculations of distortions of electronic wavefunctions, as well as for calculations using the multiscale Green function. This work will produce a detailed picture connecting lattice distortions and electronic structure in NVD, utilizing the accuracy of DFT, the directness of tight-binding, and the bridging of short and long range on the lattice from MSGF. While challenging to implement this hybrid approach, there is no reason for it to fail as a whole; any unexpected complications will be handled by making appropriate adjustments, like refining the functional within DFT, reconsidering orbital details within tight-binding, or revisiting the connections from MSGF. Each separate method is well known, but this hybrid approach is entirely new and has promising applicability. Final deliverables from this work include:

- Implementation of spin-resolved DFT for NV centers, with PBE functional and spin corrections.
- Establishment of theoretical connection between MSGF and DFT, bridging length scales.
- Development of qualitative implications for application of NV centers as qubits.

- Extension of MSGF code from NIST, using some outputs from DFT like lattice potential function.
- Code for tight-binding method, using outputs from MSGF and DFT like lattice displacements.
- Code for visualizing MSGF and tight-binding results, and combining all parts into a cohesive package.

This work and its associated code will be useful for future projects in which more complex effects in NVD may be explored, such as those due to electric and/or magnetic fields, or applied strain fields, leveraging the accuracy and multiscale nature of this proposed hybrid approach. This work may also be applied to defects in other materials relevant for quantum computing, such as NV centers in silicon carbide.

Detailed modeling enables virtual experimentation, helps plan measurements and design of experiments, and decreases the time required to bring research from lab to industry. The three-step approach outlined in this proposal will reveal the electronic structure of NVD in great detail, including spin interactions, especially clarifying the relations between electronic properties, lattice distortions, and long range strain. The effects of strain are important for realizing NVD qubits, especially since strain is influenced by crystallite size, and may be exploited for advanced metrology (electrometry). Any real application of NVD will require strain to be described in as much detail as possible, at multiple length scales, and this proposed work will develop a method for achieving that goal. Other scientists will be encouraged by such a thorough description: some will be further enabled to incorporate NVD qubits into large quantum computing architectures, while others will be able to build on existing applications of NVD for metrology.

The proposed calculations and associated computer code deliverables will advance NIST goals like measurement and characterization of modern materials. The results of this work will also find applications in American industry, particularly within the emerging quantum computing sector. The Material Measurement Laboratory will benefit from this work, since it contributes to a better understanding of the complex electronic structure of NVD and its relation to strain, enabling further experimentation and applications

of qubits using NVD. Within the Applied Chemicals and Materials Division[36], this proposed work will contribute to the characterization of materials like NVD for quantum computing, an active area of interest, particularly among researchers Vinod K. Tewary, Edward J. Garboczi, and Alex Smolyanitsky.

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