Improving DFT Methods: A tool for predicating NMR spectra and diversifying science

Proposed research:

1. Use DFT (Density Functional Theory) to calculate nuclear properties to interpret low and high concentration paramagnetic solid state NMR (Nuclear Magnetic Resonance) data. Identify shortcomings of current methods and theory within these calculations.
2. Develop improved theory, functionals, basis sets, and/or corrections to overcome these shortcomings.
3. Develop aids to facilitate broader use of DFT for NMR by non-expert user.
4. Present/publish easier-to-follow instructions and classroom ideas to expose and excite students and scientists to better understand and apply DFT methods.

Introduction:

NMR is a highly specific spectroscopic technique to observe the electronic structure of materials. A powerhouse of the molecular chemistry and biochemistry communities, NMR is scarcely used by inorganic solid materials chemists despite informative demonstrations of the technique on diverse materials like nanoparticles, lasers, catalysts, batteries, cements, and geologic materials. The technique's high specificity typically results in complex spectra that are difficult to interpret, a primary reason for its minimal use in solid state chemistry. Recently, great strides have been made in developing density functional theory (DFT) techniques[1–3] to reproduce and interpret diamagnetic NMR spectra computationally. However, DFT usually falls short of accurately predicting the spectra for paramagnetic solids (solids with unpaired electronic spins, such as those containing transition metals and lanthanides)[3,4], a significant problem since many technologically-important materials (both natural and synthetic) can be classified as paramagnetic. The problem was summarized recently: *"There is currently no methodology to predict all of the relevant interactions in paramagnetic solids at a consistent computational level."*[3]

To address the shortcomings of current computational techniques, the proposed research will (1) apply DFT to existing paramagnetic spectra to characterize specific shortcomings, (2) develop new theory to overcome these shortcomings, (3) develop a practical guide or tutorial to aid researchers

in applying this approach, and (4) develop computational chemistry approaches to broadly improve education and diversity in the physical sciences.

Characterization of shortcomings

To address the shortcomings of DFT, initial efforts will be focused on replicating experimental NMR spectra of transition metal containing oxide solids. To date, it is unclear which circumstances produce inaccurate predictions, since publications focus almost exclusively on positive, novel results and only hint at negative results[3,4]. Oxide materials present a good testing ground because there is a growing body of experimental spectra[5–14], paramagnetic concentrations range from dilute concentrations (0.01% Fe in Mg2SiO4) to major components (NiO)[15], and the most accurate theoretical predictions to date have also been made on this class of materials[16–18]. Replicating a variety of materials (e.g., simple oxides, silicates, phosphates, aluminates), coordination environments (4, 6, and 7), and donor electron cations (Mn, Fe, Co, Ni, Cu) with a diversity of bond types, angles, and lengths (all of which strongly influence the electronic structure and resulting spectra) will help generalize when and where improvements in the theory are needed.

Improved methodologies

DFT shortcomings may be due to inadequacies in the chemical theories that are applied in DFT software or from poorly selected user inputs. Improvements in theory will likely be achieved by merging existing approaches. For instance Avezac et al.[19] incorporate accurate predictions of nuclear properties generalized for metals (a closely related phenomenon to paramagnetic shifts) within the framework for predicting NMR data. Pairing this with theory developed for predicting NMR of phosphates[16–18], which focuses on accuracy for paramagnetic shifts by calculating contributions in different software codes independent of the NMR prediction[17], could help strengthen computational predictions of paramagnetic NMR. Optimizing the fine details of the calculations, such as the exchange and correlation interactions or basis sets, may also be necessary, especially since the best paramagnetic NMR results are calculated in highly optimized systems[16,17,20]. Existing application of machine learning techniques to improve such settings include learned functionals[21–23] and smaller corrections that improve overall accuracy or efficiency[24–26]. Finely tuned inputs will be developed for the specific classes of materials of interest to improve paramagnetic NMR predictions.

Scientists applying DFT methods want fast, accurate, and robust results. Running a calculation involves a wide variety of ordinal and numerical parameters (basis set, functional, cutoff, k-point grid, etc.), which must be selected with the accuracy of the investigated property in mind; these ultimately influence the final output. However, selecting optimal parameters is often not straightforward, especially for complex calculations in understudied compositions and structures. Addressing this problem is a second potential environment for machine learning. While assembling a dataset to train across multiple parameters is likely beyond the scope of this postdoc, presenting a framework for the prediction of these parameters first may better motivate the development of a consistent computational chemistry reporting format to assemble such a dataset.

Learning on machines: Using computational chemistry to create avenues for disadvantaged students to succeed.

Computational chemistry holds immense potential as a tool to progress equality and representation in the sciences. The necessary hardware (keyboards, computers, and internet connections) are already present at many minority-serving community colleges and high schools. Complete software packages such as Quantum Espresso[27] are free to download and operate. Using a computer to solve a problem with no known answer could engage and excite a variety of minds that are scarce in higher education, introduce these students to the practice of scientific research, and provide a hands on learning opportunity to grasp chemistry concepts.

Unfortunately, computational chemistry falls short of this potential, in part due to challenging barriers to entry. Many scientific publications shroud the approach's simplicity in copious acronyms, a coveted secrecy of the run files used, and incompletely described methods that require insider knowledge to reproduce. From scientific research to postdoctoral applications, access to successful examples (and lots of them) can be an important part of learning for many students[28]. To address this problem, 20% of the fellowship will be spent designing and creating example projects for undergraduate classrooms, a straightforward practical guide/tutorial for students (and teachers), and additional resources to enable the hands-on learning and research.

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