Research proposal

Mining physical properties of organic molecular crystals via Density Functional Theory calculations

By Yoon Tiem Leong

School of Physics, Universiti Sains Malaysia

March 2019

Organic molecular crystals with complex crystalline structures are routinely synthesized and characterized in the X-ray Crystallography lab in USM on a routine basis [0]. Many of the synthesized crystals are single crystals with unique crystalline structures. The crystal structures are determined via X-ray crystallography with high degree of precision in the said lab. Refs. [1], [2] are two illustrative examples of organic molecular crystals resolved by the USM X-ray Crystallography lab.

These crystals can be synthesized in the lab at a relatively lost cost via standardized procedures. More importantly, due to the organic nature of their constituent atoms, the crystal structure of organic molecular crystals can vary vastly, dependent on the details of the synthesizing procedures, chemical constituents etc. Since the electronic properties of crystalline solid materials are determined by the electronic structure at the atomic scale, which is in turn a strong function of the crystalline structure, organic molecular crystals offer a highly diversified pool of materials with nearly infinite possible electronic properties waiting to be discovered. It is a realistic anticipation that some organic crystals buried in the vast pool of synthesized materials in the X-ray Crystallography Lab, USM, may possess novel or even exotic electronic properties that make them potential functional materials.

In principle, an organic molecular crystalline is essentially a complex, many-body quantum system governed by the Schroedinger equation. A well-established first-principles computational methodology to calculate the ground state of crystalline solids (which, by definition, is periodic), from which the electronic properties can be subsequently derived, is the Nobel-prize-winning (1998) Density Functional Theory (DFT) [5,6]. It is a first-principles approach to solve quantum mechanical many-body problem. Despite its well-known expensive cost (in terms of computational resources), DFT has made it a practical feasibility to carry out numerical computations to obtain realistic properties of solid state systems [7]. In practice, the only ingredient required as the input to such calculations is the crystallographic information (such as lattice parameters, crystallography group, coordinates of the basis atoms, type of the basis atoms).

Over the years, USM X-ray Crystallography Lab has measured and published the crystallographic information of thousands of organic molecular crystals they synthesized in publicly accessible databases and journals, such as the Crystallography Open Data base [8]. The pool of molecular crystals synthesized and resolved by the USM X-ray Crystallography Lab is a potential reservoir for functional materials with novel magnetic, dielectric, thermal and catalytic properties. As an example, chalcones with chemical formula (2E)-1-(3-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one, and (2E)-3-(4-chlorophenyl)-1-(3-fluoro-4-methoxyphenyl)prop-2-en-1-one synthesized by them have been suggested to have prominent applications in optical limiting and optical switching [3,4]. In [3,4] these crystals are theoretically screened using DFT calculations to determine their non-linear optical properties.

However, due to the pragmatic fact that it is costly, time consuming and tedious to experimentally characterize these synthesized crystals, the potential preciousness of these crystals remains largely unexplored. Ref. [3] illustrates a working example of 'measuring' the non-linear optical property of a molecular crystal *in silico* via DFT calculations without actually carrying out real measurements. Such a computational approach, which are nowadays routinely performed on various crystalline systems by computational materials scientists, is a convenient and powerful way to theoretically explore the potential functionalities of these crystals. DFT can be used to computationally screen these crystals to determine their electronic properties even before they are experimental measured.

Many software packages are available to perform DFT calculations. Among the most popular ones are Gaussian [9], VASP [10] and Quantum Espresso [11]. These are the DFT packages of choice in this proposal. DFT calculations on organic molecular crystals, such as those synthesized and measured in the X-ray Crystallography Lab, was once a computationally daunting task due to its highly expensive cost (computationally speaking) that scales as $\gtrsim N^3$, where N is the number of electrons in the system. Crystalline systems of the size $\gtrsim 10^2$ atoms per unit cell (this is the scale of a typical organic molecular crystal) are thought to be too large to be practically solvable by DFT without supercomputing resources. However, recent development in GPU computing has made DFT computation for such a large crystalline system to become computationally pragmatic and affordable. Gaussian, VASP and Quantum Espresso packages are proposed as the DFT packages of choice since these versions support GPU computing capability, allowing first-principles calculations on these large molecular crystals to be performed at pragmatically affordable cost, both computationally as well as monetarily.

This proposal proposes to use existing DFT packages that are already available in the theoretical and computational physics group, school of physics, namely, Gaussian, VASP and Quantum Espresso, which are equipped with GPU computing capability, to perform first-principles calculations to screen the organic molecular crystals synthesized and published in public domain by USM Crystallography Lab. By systematically screening the published crystals data bases via routine GPU-capable DFT calculations, selected physical properties of interest, such as thermal, vibrational, electric, magnetic, linear and non-linear optical properties can be determined *in silico*. The results of these DFT calculations could be a valuable resource to pave the way of discovering potentially useful or even exotic properties among these crystals as functional materials. Screening these materials via DFT calculations required very specific knowledge in terms of theoretical knowledge and computational know-how to manipulate the DFT packages, which is our expertise

Apart from the above technically-specific plan, this proposal also wishes to establish a DFT-training initiative that sees a close collaboration between the theoretical and computational physics group (in which the group leader, Dr. Yoon, is an expert in DFT calculations) and the X-ray crystallography research group (in which Dr. Quah is an expert in experimental synthesis and characterization of molecular crystals). The merging of both expertise (i.e., ab-initio calculations and experiments) can accelerate the production of high-quality research output that combines both aspects. This proposal wishes to champion such collaborative research model which is very rare in local research institutions. In addition, it is also proposed to initiate a systematic training project to train up the graduate students and academic members in the X-rays crystallography to master the use of *ab-initio* calculations (i.e., DFT). With the establishment of the systematical training program, the researches in the X-ray Crystallography Lab will be able to nurture its own DFT expertise that will definitely raise the par of the research quality in the School of Physics in the long run.

References

[0] Refer to the USM School of Physics X-ray Crystallography research lab URL at http://www.fizik.usm.my/index.php/senior-lecturer/224-quah-ching-kheng

[1] Huey Chong Kwong, Siau Hui Mah, Tze Shyang Chia, Ching Kheng Quah and C. S. Chidan Kumar, Cholinesterases Inhibitory Activities of Adamantyl-Based Derivatives and Their Molecular Docking Studies, Molecules (2017). 22, 1005.

[2] Farzin Marandi, Keyvan Moeini, Sakineh Ghasemzadeh, Zahra Mardani, Ching Kheng Quah and Wan-Sin Loh, Synthesis, spectral and X-ray diffraction of two new 2D lead(II) coordination polymers formed by nicotinic acid N-oxide linkers, Journal of Molecular Structure (2017). 184, 342–354

[3] T. Chandra Shekhara Shetty et. al, Optical nonlinearity of D-A-p-D and D-A-p-A type of new chalcones for potential applications in optical limiting and density functional theory studies, Journal of Molecular Structure 1143 (2017) 306–317.

[4] Shivaraj R. Maidur, P.S. Patil, Anusha Ekbote, Tze Shyang Chia and Ching Kheng Quah, Molecular structure, second- and third-order nonlinear optical properties and DFT studies of a novel non-centrosymmetric chalcone derivative: (2E)-3-(4-fluorophenyl)-1-(4-{[(1E)-(4-fluorophenyl)methylene]amino}phenyl)prop-2-en-1-one, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2017). 184, 342-354.

[5] W. Kohn and L.J. Sham, "Self–consistent equations including exchange and correlation effects," Phys. Rev. A. 140, 1133 (1965).

[6] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev. B 136, 864 (1964).

[7] For a very useful text book for practical implementation of DFT computation in condensed matter physics, see e.g. Richard M. Martin, Electronic Structure: Basic Theory and Practical Methods, Cambridge University Press (2004).

[8] http://www.crystallography.net/cod/search.html

[9] Gaussian webpage, http://gaussian.com/dft/

[10] VASP webpage, https://www.vasp.at/

[11] Quantum Espresso webpage, https://www.quantum-espresso.org/

Milestones (12 moths)

1. 4th month - Submission of the first article for publication in a selected ISI research journal in Q1 quartile.
2. 8th month - Submission of the first article for publication in a selected ISI research journal in Q1 quartile.
3. 12th month - Submission of the first article for publication in a selected ISI research journal in Q1 quartile.
4. 16th month, Submission of the first article for publication in a selected ISI research journal in Q1 quartile.
5. 20th month - Submission of the first article for publication in a selected ISI research journal in Q1 quartile.
6. 24th month - Submission of the first article for publication in a selected ISI research journal in Q1 quartile.