Final Report

Project Title: Non-Empirical and Self-Interaction Corrections for DFTB: Towards Accurate Quantum Simulations for Large Mesoscale Systems

University of California, Riverside (legal name: The Regents of the University of California on behalf of its Riverside campus)
c/o Office of Research and Economic Development
200 University Office Building
Riverside, CA 92521

DUNS number: 62-779-7426

Principal Investigator: Prof. Bryan M. Wong

Phone: (951) 827-2163
Email: bryan.wong@ucr.edu
Webpage: http://www.bmwong-group.com

1. Abstract/Executive Summary

This project was comprised of two complementary (but parallel) thrusts: (1) implementing massively-parallelized computing hardware (with new computational hardware that may replace GPUs) in the density functional tight binding (DFTB) approach and (2) developing new capabilities in DFTB to calculate the electronic structure and dynamics of large chemical systems. While classical molecular dynamics can handle hundreds of thousands of atoms, it cannot provide a first-principles based description of chemical systems at the quantum level. At the other extreme, conventional Kohn-Sham DFT methods can probe the true quantum mechanical nature of chemical systems; however, these methods cannot tackle the large sizes and length scales relevant to dynamics simulations of realistic systems. The DFTB formalism utilized in this project provides a viable approach for probing these large systems at a quantum mechanical level of detail. However, to utilize the DFTB approach for accurate calculations of electronic properties, it is crucial to incorporate *quantum-based corrections* in DFTB since exchange-correlation effects can still remain very strong in these large systems. At the same time, enhancing the computational efficiency of DFTB is also essential since optimal computational performance is required for addressing the large size scales associated with realistic chemical systems. As such, the new non-empirical corrections and computing hardware enhancements implemented in this project will enable accurate *and* computationally efficient approaches to directly probe electronic properties in these large, complex systems.

2. Impact

This project was the result of a DOE Early Career Award that the PI was awarded in 2016, which was jointly funded by the Condensed Phase & Interfacial Molecular Science (CPIMS) and Computational & Theoretical Chemistry (CTC) DOE-BES programs. During the past 5 years of this award, the PI carried out large-scale calculations of various chemical/material systems, which resulted in 21 published journal articles[1-21] and 4 additional manuscripts in press.[22-25] Most of these DOE-supported papers have been published in the *Journal of Chemical Theory and Computation* (*JCTC*), which is the premier ACS journal for computational/theoretical work. Other papers resulting from this award have been published in high-impact journals such as *PNAS*, *Advanced Optical Materials*, *Nature Communications*, and *Advanced Materials*. In addition, several of these DOE-supported papers have been featured on the cover[5, 10, 14, 16, 19, 21] (see **Fig. 1**) or selected by the editor as an "important paper" or "Editor's Suggestion."[5, 15, 21] A selected portion of these papers is briefly highlighted here: **(1) Hardware/Software Development:** Recently, the PI

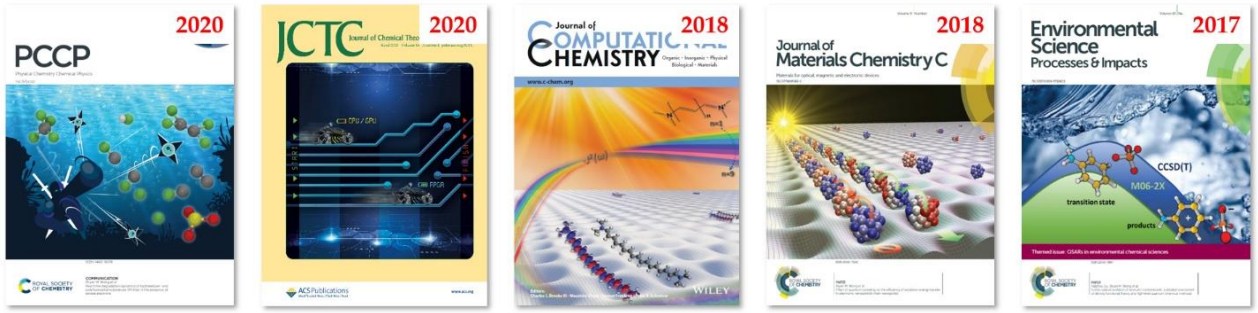

Fig. 1. Selected papers featured as cover articles, which acknowledge and were supported by the PI's DOE Early Career Award from 2016-2021.

published the first application of field-programmable gate arrays (FPGAs) as new, customizable hardware architectures for carrying out fast and energy-efficient quantum dynamics simulations. FPGAs allow for the customization of hardware *at the level of specific electrical signals in the circuit* to give a truly optimized computational performance. Most notably, the PI showed that the computational performance of FPGAs exceeds that of optimized commercial mathematical libraries running on high-performance GPUs and consumes 4 times less energy than modern GPU or CPU architectures.[19] **(2) Real-Time Electron Dynamics:** Using real-time, time-dependent density functional theory (RT-TDDFT) approaches, the PI's group explored the electron dynamics of complex chemical/material systems, including long-range electronic excitation transfer in plasmonic nanoantennas[1, 4, 10] excitons in 2D materials,[15] carrier dynamics in tellurium nanosheets,[17] and chromophores in intense magnetic fields.[18] **(3) Understanding Theoretical Limitations of DFT Methods:** In a series of papers, the PI explored the theoretical limitations, accuracy, and caveats of DFT methods in various systems, including the historically difficult computation of electron affinities/unbound anions,[2] higher-order electronic properties of molecules,[14] intricate halogen bonding interactions,[7] fractional occupation numbers in self-interaction corrected approaches,[16] and limitations of DFT in challenging chemical systems.[6] This project builds upon these prior experiences of the PI to expand their approaches to RT-TDDFT calculations for optically-driven reactions on complex interfaces.

In the latter half of 2019, we utilized time-dependent density functional theory to understand exciton condensation in titanium diselenide ($TiSe_2$), which is a prototypical material for experimentally observing emergent properties from many-body quantum effects. Specifically, our work in this area provided the first ab initio atomic-level framework for rationalizing recent experiments and further manipulation exciton condensates in $TiSe_2$. This paper was selected by the editors as a Physical Review B Editors' Suggestion as one of "a small number of PRB papers that the editors and referees find of particular interest, importance, or clarity." This paper was also featured prominently on the American Physical Society (APS) website at https://journals.aps.org/prb/highlights.

Also in 2020, we utilized both self-interaction-corrected DFT and ab initio molecular dynamics to understand the degradation dynamics of chemical contaminants (known as per- and polyfluoroalkyl substances [PFASs]) in water. In particular, we provided the first real-time dynamic simulation and prediction of PFAS using excess electrons in aqueous phases. This work garnered immense attention from the scientific society, which included news coverage from the Royal Society of Chemistry in ChemistryWorld (https://www.chemistryworld.com/news/excess-electrons-can-degrade-polluting-fluorinated-compounds-simulations-find/4011182.article) as well as highlighted by the DOE Office of Science. Additional attention to this paper included being featured as the front cover for the April 7, 2020 issue of Physical Chemistry Chemical Physics (http://dx.doi.org/10.1039/D0CP90075C), selected by the editors to appear in the 2020 PCCP HOT Articles Themed Collection of Physical Chemistry Chemical Physics as a "hottest work published in PCCP" (https://pubs.rsc.org/en/journals/articlecollectionlanding?sercode=cp&themeid=82b7cc99-4e0c-4c4a-bb00-a57a776e3a9c), and featured as "Chemistry News" in Phys.org (https://phys.org/news/2020-03-chemicals.html)

The PI's work has also been recognized by the DOE Office of Science, with two of his recent publications featured as Science Highlights on the official DOE-BES main website (**Fig. 2**).[26-27] *Several of the postdocs supported by the PI's DOE Early Career Award have already started their own independent careers as faculty members in academia or senior scientists*: (1) Sharma

S.R.K.C. Yamijala (former postdoc from 2018-2020) is currently an assistant professor at IIT Madras (a highly-ranked engineering university in India); (2) M. Belén Oviedo (former postdoc from 2014-2016) is currently an assistant professor at the Universidad Nacional de Córdoba in her home country of Argentina; (3) Fredy Aquino (former postdoc from 2016-2019) is a software engineer at QSimulate, a quantum computing startup led by Toru Shiozaki, a former CTC DOE-BES PI. In addition, the graduate students in the PI's group had extensive experience with developing and running large-scale, time-dependent quantum calculations. During the time of this award, graduate students in the PI's group have been recognized by the American Chemical Society as finalists for the NVIDIA GPU Award.[28] As such, this award/grant enabled new computational efforts to have a strong and broad impact on DOE-BES applications to understand dynamics in *real* chemical and material systems.

Fig. 2. DOE BES website highlighting the PI's recent 2019 work on time-dependent quantum dynamics of energy transfer in large nanoparticle assemblies.

In terms of human resources, this DOE Grant has provided formal mentorship between the PI and the participants supported by this project which include 3 Postdoctoral Associates, 2 PhD students, and 2 MS students. The 2 MS theses were completed in 2017, and 1 PhD thesis completed in June 2018.

In terms of impact on society beyond science and technology, this project enabled a deep understanding of energy transfer processes that can be used to enhance modern society beyond the technological applications mentioned above. As an example, the large systems probed in this project can enable a deeper understanding of complex mesosystems, with the opportunity to deeply understand the real-time electron dynamics approaches developed in this project. In addition, this project provides new approaches to start answering several intriguing scientific questions: How are electronic effects utilized and exploited in large systems (such as self-assembled nanomaterials or biomaterials)? How important are quantum effects in these systems, and are these unusual observations sensitive to exchange-correlation effects? To answer these questions, a more fundamental understanding of the dynamics of these systems is required, and investigating these issues with the techniques in this DOE project will allow us to probe these effects to benefit societal needs, such as energy storage, transfer, and production.

The DOE reporting requirements state "STI that is publicly accessible need not be duplicated in the report if a citation with a link to where the information may be found is included in the report." To comply with this mandate, all of the technical details and papers generated from this grant can be viewed on DOE's Public Access Gateway for Energy and Science (http://www.osti.gov/pages). This work was supported by the U.S. Department of Energy, Office of Science, Early Career Research Program under Award No. DE-SC0016269.

References

1. Alvarez Barragan, A.; Ilawe, N. V.; Zhong, L.; Wong, B. M.; Mangolini, L., A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles. *The Journal of Physical Chemistry C* **2017,** *121* (4), 2316-2322.
2. Anderson, L. N.; Oviedo, M. B.; Wong, B. M., Accurate Electron Affinities and Orbital Energies of Anions from a Nonempirically Tuned Range-Separated Density Functional Theory Approach. *Journal of Chemical Theory and Computation* **2017,** *13* (4), 1656-1666.
3. Cao, Y.; Morrissey, T. G.; Acome, E.; Allec, S. I.; Wong, B. M.; Keplinger, C.; Wang, C., A Transparent, Self-Healing, Highly Stretchable Ionic Conductor. *Advanced Materials* **2017,** *29* (10), 1605099.
4. Ilawe, N. V.; Oviedo, M. B.; Wong, B. M., Real-Time Quantum Dynamics of Long-Range Electronic Excitation Transfer in Plasmonic Nanoantennas. *Journal of Chemical Theory and Computation* **2017,** *13* (8), 3442-3454.
5. Pari, S.; Wang, I. A.; Liu, H.; Wong, B. M., Sulfate radical oxidation of aromatic contaminants: a detailed assessment of density functional theory and high-level quantum chemical methods. *Environmental Science: Processes & Impacts* **2017,** *19* (3), 395-404.
6. Ali, Z. A.; Aquino, F. W.; Wong, B. M., The diamine cation is not a chemical example where density functional theory fails. *Nature Communications* **2018,** *9* (1), 4733.
7. Anderson, L. N.; Aquino, F. W.; Raeber, A. E.; Chen, X.; Wong, B. M., Halogen Bonding Interactions: Revised Benchmarks and a New Assessment of Exchange vs Dispersion. *Journal of Chemical Theory and Computation* **2018,** *14* (1), 180-190.
8. Aquino, F. W.; Wong, B. M., Additional Insights between Fermi–Löwdin Orbital SIC and the Localization Equation Constraints in SIC-DFT. *The Journal of Physical Chemistry Letters* **2018,** *9* (22), 6456-6462.
9. Cao, Y.; Wu, H.; Allec, S. I.; Wong, B. M.; Nguyen, D.-S.; Wang, C., A Highly Stretchy, Transparent Elastomer with the Capability to Automatically Self-Heal Underwater. *Advanced Materials* **2018,** *30* (49), 1804602.
10. Ilawe, N. V.; Oviedo, M. B.; Wong, B. M., Effect of quantum tunneling on the efficiency of excitation energy transfer in plasmonic nanoparticle chain waveguides. *Journal of Materials Chemistry C* **2018,** *6* (22), 5857-5864.
11. Rhaman, M. M.; Hasan, M. H.; Alamgir, A.; Xu, L.; Powell, D. R.; Wong, B. M.; Tandon, R.; Hossain, M. A., Highly selective and sensitive macrocycle-based dinuclear foldamer for fluorometric and colorimetric sensing of citrate in water. *Scientific Reports* **2018,** *8* (1), 286.
12. Sulas, D. B.; London, A. E.; Huang, L.; Xu, L.; Wu, Z.; Ng, T. N.; Wong, B. M.; Schlenker, C. W.; Azoulay, J. D.; Sfeir, M. Y., Preferential Charge Generation at Aggregate Sites in Narrow Band Gap Infrared Photoresponsive Polymer Semiconductors. *Advanced Optical Materials* **2018,** *6* (7), 1701138.
13. Woodard, A.; Xu, L.; Barragan, A. A.; Nava, G.; Wong, B. M.; Mangolini, L., On the non-thermal plasma synthesis of nickel nanoparticles. *Plasma Processes and Polymers* **2018,** *15* (1), 1700104.
14. Xu, L.; Kumar, A.; Wong, B. M., Linear polarizabilities and second hyperpolarizabilities of streptocyanines: Results from broken-Symmetry DFT and new CCSD(T) benchmarks. *Journal of Computational Chemistry* **2018,** *39* (28), 2350-2359.
15. Lian, C.; Ali, Z. A.; Wong, B. M., Charge density wave hampers exciton condensation in 1T-$TiSe_2$. *Physical Review B* **2019,** *100* (20), 205423.

16. Aquino, F. W.; Shinde, R.; Wong, B. M., Fractional occupation numbers and self-interaction correction-scaling methods with the Fermi-Löwdin orbital self-interaction correction approach. *Journal of Computational Chemistry* **2020,** *41* (12), 1200-1208.
17. Jnawali, G.; Xiang, Y.; Linser, S. M.; Shojaei, I. A.; Wang, R.; Qiu, G.; Lian, C.; Wong, B. M.; Wu, W.; Ye, P. D.; Leng, Y.; Jackson, H. E.; Smith, L. M., Ultrafast photoinduced band splitting and carrier dynamics in chiral tellurium nanosheets. *Nature Communications* **2020,** *11* (1), 3991.
18. Kudisch, B.; Maiuri, M.; Moretti, L.; Oviedo, M. B.; Wang, L.; Oblinsky, D. G.; Prud'homme, R. K.; Wong, B. M.; McGill, S. A.; Scholes, G. D., Ring currents modulate optoelectronic properties of aromatic chromophores at 25 T. *Proceedings of the National Academy of Sciences* **2020,** *117* (21), 11289-11298.
19. Rodríguez-Borbón, J. M.; Kalantar, A.; Yamijala, S. S. R. K. C.; Oviedo, M. B.; Najjar, W.; Wong, B. M., Field Programmable Gate Arrays for Enhancing the Speed and Energy Efficiency of Quantum Dynamics Simulations. *Journal of Chemical Theory and Computation* **2020,** *16* (4), 2085-2098.
20. Shinde, R.; Yamijala, S. S. R. K. C.; Wong, B. M., Improved band gaps and structural properties from Wannier–Fermi–Löwdin self-interaction corrections for periodic systems. *Journal of Physics: Condensed Matter* **2020,** *33* (11), 115501.
21. Yamijala, S. S. R. K. C.; Shinde, R.; Wong, B. M., Real-time degradation dynamics of hydrated per- and polyfluoroalkyl substances (PFASs) in the presence of excess electrons. *Physical Chemistry Chemical Physics* **2020,** *22* (13), 6804-6808.
22. Yamijala, S. S. R. K. C.; Oviedo, M. B.; Wong, B. M., Density Functional Tight Binding Calculations for Probing Electronic-Excited States of Large Systems. *Reviews in Computational Chemistry* **2021,** *Accepted*, In Press.
23. Ma, X.; Liu, Q.; Yu, N.; Xu, D.; Kim, S.; Liu, Z.; Jiang, K.; Wong, B. M.; Yan, R.; Liu, M., 6 nm Super-Resolution Optical Transmission and Scattering Spectroscopic Imaging of Carbon Nanotubes Using a Nanometer-Scale White Light Source. *Nature Communications* **2021,** *12*, 6868.
24. Biswas, S.; Wong, B. M., Ab Initio Metadynamics Calculations Reveal Complex Interfacial Effects in Acetic Acid Deprotonation Dynamics. *Journal of Molecular Liquids* **2021,** *330*, 115624.
25. Yamijala, S. S. R. K. C.; Kwon, H.; Guo, J.; Wong, B. M., Stability of Calcium Ion Battery Electrolytes: Predictions from Large-Scale Ab Initio Molecular Dynamics Simulations. *ACS Applied Materials & Interfaces* **2021,** *13*, 13114-13122.
26. How to Best Predict Chemical Reactions of Contaminants in Water. https://www.energy.gov/science/bes/articles/how-best-predict-chemical-reactions-contaminants-water-0 (accessed 05/20/2019).
27. Too Close for Comfort: Nanoparticles Need Some Space to Transfer Energy. https://www.energy.gov/science/bes/articles/too-close-comfort-nanoparticles-need-some-space-transfer-energy (accessed 05/20/2019).
28. The NVIDIA GPU Award for Best GPU Poster Finalists for Denver (spring 2015). https://www.acscomp.org/comp-news/archives/2015/thenvidiagpuawardforbestgpuposterfinalistsfordenverspring2015 (accessed 02/02/2021).