High-Performance Computing and Data Science in Materials for renewable energy science

by

Pavan Kumar Behara

August 31, 2020

A dissertation submitted to the faculty of the Graduate School of the University at Buffalo, The State University of New York in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Computational and Data enabled Science and Engineering program



www.manaraa.com

ProQuest Number: 28031012

All rights reserved

INFORMATION TO ALL USERS The quality of this reproduction is dependent on the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 28031012

Published by ProQuest LLC (2020). Copyright of the Dissertation is held by the Author.

All Rights Reserved. This work is protected against unauthorized copying under Title 17, United States Code Microform Edition © ProQuest LLC.

> ProQuest LLC 789 East Eisenhower Parkway P.O. Box 1346 Ann Arbor, MI 48106 - 1346



Copyright by

Pavan Kumar Behara

2020

All Rights Reserved



I dedicate this work to my parents, Sri Ramachandra Murthy and Lakshmi, and my sister Prathibha Sakunthala and my cousin Priyadarshini for their love and constant support.



Acknowledgements

I would like to express heartfelt gratitude to my advisor Prof. Michel Dupuis for the whole learning process, support and timely remarks on my work. Thanks for guiding me at every step and for being so patient with all my doubts however naive they might be and always helping with a wide smile. Thanks for being there when I am confused and changing my worldview. Furthermore, I would like to thank the professors who taught me and made the UB experience worthwhile both in CBE as well as CDSE programs. I thank my thesis committee Prof. Olga Wodo, Prof. Jaroslaw Zola and Prof. Johannes Hachmann for providing guidance during early years of my PhD and reviewing my work. I would like to thank Dr. Andrew Schultz for helping me with the dynamics portion of my thesis. I want to thank Prof. David Kofke for his support and mentorship during my masters and beyond. I would like to thank my previous mentor Dr. Kumaresan Thangaraj for his professional advice and warmth. I would also like to extend my thanks to Dr. Ashish Gujarathi for his mentorship during the early stages of my career.

I thank my fellow lab mates for keeping me company in exploring the land of the lost. Especially, Dr. Nina Tyminska for helping me during my initial phase. I thank the Dupuis group members Viswanath, Xiaoyu, Christine, Dan, Bingan, Yuhan, Yang, Xiuting for their amazing company.

I thank Gopichand, Karnesh, Aditi, Atif, Prakhar, Prashanth, Saurabh Singh, Priti and Snehal Rane for making life in Buffalo beautiful. And to my family, all the Beharas, Mocherlas and Mallapragadas, I will be grateful forever for your love. Special thanks to Mukesh Kiran, Karthik Bagade, and Vishnu Teja for their never-ending affection.



iv

Abstract

Solar energy conversion to fuels via photo-electro-catalysis or to electricity via photovoltaics involves charge carriers (electrons and holes) that diffuse through the light harvesting material. Materials based on inexpensive and abundant transition metals are potentially great absorbers of solar light in the visible range. However, the main bottleneck to efficiency is slow charge carrier transport in these materials, a deficiency whose understanding and remediation requires atomistic level investigations. My research work is focused on the determination of carrier mobility in photo-active transition metal-based semiconductors and about finding correlations with their chemical compositions and structures. This work involves developing novel tools and approaches to characterize charge transfer in periodic crystalline systems.

Marcus/Holstein theory of electron transfer (ET) models these fundamental processes as a barrier crossing mechanism and the developments includes new ways of estimating the kinetic rate parameters. We implemented a new modeling capability for the calculation of the electronic coupling transition element V_{AB} in CP2K, a widely used *ab initio* package in materials research community. This development opens the full characterization of electron transfer in the solid state. The approach is valid for any single-determinant wavefunction with localized character representing the electronic structure of the system, from Hartree-Fock (HF) theory, to density functional theory (DFT), and others.

Secondly, we carried out a new implementation for the periodic DFT formulation of the Maximal Orbital Analysis (MOA), a wavefunction analysis method in CP2K. This method of analysis helps in the characterization of super-exchange interactions in ET. Given a wavefunction, the MOA method defines the maximal projection of the wavefunction onto a subgroup of atoms. How much the tail of a "localized" state wavefunction of a charge carrier spreads onto linker



v

bridge fragments, defines the extent of coupling and can be ascertained with fragment-wise projections, as performed in MOA.

Another contribution includes simulating polaron hopping dynamics directly (without resorting to the Marcus/Holstein model) and evaluating the activation barrier from the sampled potential energy surface. Since ET is a rare-event, accelerated molecular dynamics methods viz., hyperdynamics and metadynamics, are needed. The bond length changes can be utilized to define a reduced variable space to propagate the dynamics and limiting the phase-space sampling to critical areas. The approach removes any assumptions involved in the charge transfer model described previously.

Within the same theme, an alternate way of extracting charge transfer kinetic rates from ab initio molecular dynamics (AIMD) might be via the determination of vibrational modes and frequency spectra. Finding the frequency of the breathing phonon mode involved in the bond stretches and compressions around the charge localized site and its neighbors can give an estimate of the activation barrier. Post-processing of the molecular dynamics data through Fourier transform of velocity autocorrelation function gives the vibrational spectrum. Compressed sensing is a sparse signal reconstruction method, that has the potentially to be a more computationally-efficient alternative to Fourier transform. It is explored in this research. The approach gives somewhat of a better and faster resolved spectrum with shorter AIMD trajectories, but the density of vibrational states remains a challenge in the use of the method.

The overall aim of developing these methods is to screen materials based on charge transport and to arrive at design principles. We accumulated data on polaron transfer barriers to find various factors that drive charge transport. Establishing correlations between chemical descriptors (such as phonon frequency, elemental ionization potential, electronegativity, and others) with carrier



vi

mobility can help in rational design of energy conversion materials and was attempted. The limited number of data points remains a challenge.

Finally, an application of density functional theory to determine the efficacy of covellite (CuS) nanoplatelets for water splitting is demonstrated. Oxygen reduction reaction (ORR) pathways and electrochemical activity are determined for different surface terminations.



TABLE OF CONTENTS

Acknowledgements iv
Abstractv
List of Tables xi
List of Figures xiv
Chapter 1 Introduction
1.1 Materials Genome Initiative1
1.2 Climate Change and MGI
1.3 Materials for Green Energy and Catalysis4
1.4 Purpose of the study and methodology
Chapter 2 Electronic coupling calculation in periodic systems
2.1 Introduction11
2.2 Formulation and Implementation14
2.2.1 Considerations about localized states and VAB calculations
2.2.2 Energy calculation and contributing terms in CP2K
2.2.3 Implementation in CP2K
2.3 Application Examples
2.3.1 He ₂ ⁺ dimer
$2.3.1 \text{ He}_2^+ \text{ dimer}$
$\begin{array}{c} 2.3.1 \ \text{He}_2{}^+ \ \text{dimer}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$



Chapter 3 Maximal Orbital Analysis: Superexchange interactions in solid state	43
3.1 Introduction	43
3.2 MOA Formulation and Implementation	44
3.3 Results and Discussion	46
3.3.1 Water-dimer	
3.3.2 TiO2 system	
3.3.3 Hematite Fe_2O_3	55
3.3.4 1D-Fe ^(III) Chain – 7 units	59
3.3.5 Bismuth Vanadate (BiVO ₄)	63
3.4 Conclusion	66
Appendix	67
Chapter 4 Biased-dynamics for Electron Transfer	68
4.1 Introduction	68
4.2 Biased dynamics for polaron hopping	69
4.3 Hyperparameters and computational details	76
4.4 Results and Discussion	78
4.5 Conclusion	82
Chapter 5 Compressed Sensing for phonon modes of charge transfer	
5.1 Introduction	
5.2 Compressed sensing	
5.3 CS for resolution of ET phonon modes	86
5.4 Conclusion	95
Chapter 6 Materials Screening Based on Electron Transport	96
6.1 Introduction	96
6.2 BMX ₃ dataset	97



6.3 Chemical Descriptors for ET103
6.3.1 Multicollinearity among descriptors and feature selection
6.4 Model comparison and Results106
6.5 Prediction framework for new materials109
6.5 Conclusion112
Chapter 7 Modeling ORR in CuS pertinent to Water splitting113
7.1 Introduction113
7.2 Covellite structure
7.3 Calculation details115
7.4 DFT-Calculated Oxygen Adsorption Energy and Facet-Dependent ORR Behavior116
7.5 Conclusion
Chapter 8 Summary and Outlook
8.1 Conclusions122
8.2 Outlook
References



List of Tables

Table 2-1. Outline of one-electron, two-electron, and nuclear energy contributions obtainedby splitting the subroutine calls within the 'quick-step' code and its construction of the Kohn-Sham matrix in CP2K.25
Table 2-2 Speedup that can be achieved per step if HF treatment is replaced with DFT leveltheory for VAB calculation.29
Table 2-3. He2 + electronic coupling calculated in CP2K via the COT method with HForbitals, compared with HONDO values for the same method.32
Table 2-4. Electronic coupling V_{AB} and overlap S_{AB} calculated for $Zn2$ + with CP2K via the COT method using HF orbitals in this work, compared to cDFT orbitals in ref. 109 and the GMH formalism in ref. 97
Table 2-5. V_{AB} for ET of an electron polaron in a 1D periodic chain $[Fe(OH)_2(H2O)_2^{(+)}]_n$ with n=7, 9, and 11 units calculated with the HF level of theory. ΔG^* is the relative energy of the mid-point along the reaction pathway, λ is the reorganization energy, V _{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$)
Table 2-6. V _{AB} for a periodic chain of 7-units [Fe(OH) ₂ (H2O) ₂ ⁽⁺⁾] ₇ calculated with BLYP+U orbitals and different +U value. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, V _{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - \mathbf{V}_{AB}$)
Table 2-7. V_{AB} for electron transfer in basal plane for bulk hematite from BLYP+U orbitals using CP2K. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, V _{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$)
Table 2-8. V_{AB} for electron transfer in the c-direction for bulk TiO ₂ from PBE+U orbitals. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, V_{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$) 40
Table 2-9. V_{AB} for electron transfer in the (021) direction in bulk BiVO ₄ from PBE+U orbitals. ΔG^* is the energy of the mid-point along the hopping pathway, λ is the reorganization energy, V_{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$).
Table 3-1. MOA occupations in water dimer at HF(6-31G**) optimized geometry
Table 3-2. Number of basis functions in different basis for Ti and O. 48
Table 3-3. Population, charge, and spin from MOA for the specified atom fragments when all the molecular orbitals are projected on their respective basis functions within SZV



Table 3-4. MOA occupations when all orbitals are projected on the Ti atom which is a target for electron localization. An excess electron in alpha channel is marked in red for the charge localized state.	50
Table 3-5. MOA occupations when all orbitals are projected on the bridging O atoms involved in ET. Since all the orbitals are filled no significant difference can be observed here between neutral and charged states	51
Table 3-6. MOA with only the excess electron orbital projected onto the different fragments in SZV, DZV, and DZVP bases	52
Table 3-7. Eigen vector components corresponding to the excess orbital projection onto the basis of two bridging oxygens.	54
Table 3-8. MOA occupations along a Marcus curve for qualitative analysis. Increase in electron sharing is observed between the state0 and crossing point geometries. It is more evident with lower +U value.	55
Table 3-9. MOA occupations comparison between neutral and electron-localized states for Hematite.	56
Table 3-10. MOA occupations for all orbitals projection onto electron localized iron atom both before and after excess electron is introduced. Alpha orb #4 marked in red indicates the excess electron whose orbital is shown in figure 6.	57
Table 3-11. MOA occupations for all orbitals projection onto the basis function of bridging oxygen atoms. Unfilled beta orbital #9 marked in red shows significant difference with the neutral system and is assumed to facilitate superexchange for ET	59
Table 3-12. MOA occupations comparison between neutral and electron-localized states for 1d-Fe chain	60
Table 3-13 MOA occupations for all orbitals projection onto electron localized iron atom both before and after excess electron is introduced. Beta orb #4 marked in red indicates the excess electron whose orbital is shown in figure 7	61
Table 3-14. MOA occupations for all orbitals projection onto the oxygen bridge basis functions. Beta orb #9 marked in red is the highest occupation unfilled orbital and is assumed to involve in superexchange, it is shown in figure 7	63
Table 3-15. MOA occupations for the projection of all orbitals onto basis functions of Vanadium and Oxygen fragments involved in ET.	64
Table 3-16. MOA occupations for the projection of all orbitals on the basis functions of Vanadium atom targeted for electron localization before and after introduction of excess electron	65



Table 3-17. MOA occupations for projection of excess electron orbital onto the basis functions of listed atomic fragments
Table 4-1. Collective variable values in initial and final states 73
Table 6-1. Electron polaron activation barriers collected from literature
Table 6-2 Top 10 descriptors and sorted according to their variance inflation factors 106
Table 6-3 Mean-squared error for the whole dataset with different models
Table 6-4 Performance of Gradient boosting model when n-1 data points are used for training and tested on the remaining one point. Average mean absolute error for all the possible combinations is presented here and it is close to $3k_BT$
Table 7-1 Zero Point Energy Corrections and Entropic Contributions to the Free Energies 115
Table 7-2 Oxygen molecule adsorption energies on different sites
Table 7-3 Step energy and overpotential for ORR associative and dissociative mechanisms 120



List of Figures

Figure 1-1. US government infographic on Materials Genome Initiative (MGI) from policy website (url: www.mgi.gov)
Figure 1-2. The American Society for Testing and Materials (ASTM) G-173 spectra represent terrestrial solar spectral irradiance on a surface of specified orientation under US standard atmosphere. Major portion of solar radiation is in visible range of 400-700 nm, shaded in rainbow color
Figure 1-3. A simple diagram depicting Marcus electron transfer pathway between states A and B, wherein an activation barrier E_a and electronic coupling matrix element V_{AB} are labeled
Figure 2-1. Spin density of an electron polaron localized on a Ti site in TiO2. We aim to calculate the rate for the polaron to hop between two Ti sites. The blue spheres are polaronic Ti atoms, the red spheres are O atoms, and the silver spheres are Ti atoms
Figure 2-2. Schematic of the two-well potential energy surface associated with electron or hole transfer in molecules and in the solid state (reproduced from Farazdel et al. [71]). The solid curves are the adiabatic surfaces; the dashed lines depict the diabatic states. Q_A and Q_B are the equilibrium coordinates of the A state and B state, and Q_c represent the coordinates of the lowest energy structure on the crossing seam of the diabatic surfaces. λ is the reorganization energy, $ \Delta E $ is the exothermicity of the electron transfer, E_d is the diabatic activation energy, $and V_{AB}$ is the electronic coupling between states A and B.
Figure 2-3 Speedup showing strong-scaling performance in V _{AB} calculation
Figure 2-4 Computation time with respect to increase in processors
Figure 2-5. <i>He</i> 2 + electronic coupling calculated in CP2K via the COT method with HF orbitals, compared with HONDO values for the same method
Figure 2-6. Electronic coupling V_{AB} and overlap S_{AB} calculated for $Zn2$ + with CP2K via the COT method using HF orbitals in this work, compared to cDFT orbitals in ref. 109 and the GMH formalism in ref. 97
Figure 2-7. Structure of the ferric oxide 1D-model with 7 units. The system is periodic. The excess electron is localized on the third Fe atom in state A and transfers to the fourth Fe atom in state B (as depicted with the blue arrow). The orange spheres are Fe atoms, the red spheres are O atoms, and the white spheres are H atoms
Figure 2-8 Fe-OH bonds along the chain. The localized excess electron is at position 0 . The distances in the 7- and 9-unit systems are not distinguishable from those of the 11-unit system. 36



Figure 2-9. Fe ₂ O ₃ hematite supercell with layers of spin-up [cyan \blacksquare] and spin-down [green \blacksquare] densities on Fe ^{III} atoms. The hop between two Fe atoms in a basal plane is marked in blue color. For clarity, the spin density contours are turned off for the down spin in the top picture. The orange spheres are Fe atoms, the red spheres are O atoms.	38
Figure 2-10 Rutile TiO_2 with an iso-surface of the spin density of an electron localized on a Ti atom. The hop between two Ti atoms is marked in blue color in the [001] direction. The silver spheres are Ti atoms, the red spheres are O atoms, green spheres are the polaronic Ti atoms.	39
Figure 2-11 ms-BiVO4 with an iso-surface of spin density for an electron localized at a V atom. The hop between two V atoms is indicated in blue color. The green spheres are polaronic V atoms, silver spheres are V atoms, the red spheres are O atoms, and purple spheres are Bi atoms.	41
Figure 3-1. Water dimer with the hydrogen bond depicted by a dotted red line between the donor on the left and the acceptor on the right.	46
Figure 3-2. MOA orbitals #5 and #6, in spherical harmonic basis, for the donor water molecule. Orbital #5 on the left is a OH (σ) orbital, and #6 is a OH (σ *) orbital that has a node between the oxygen and hydrogen involved in h-bonding.	47
Figure 3-3. Bulk rutile TiO2. We are interested in looking at the electron sharing when it is localized on one of the Ti atoms highlighted here	49
Figure 3-4. MOA orbital of the excess electron when projected onto the electron-localized Ti basis functions within SZV, DZV, DZVP.	52
Figure 3-5 MOA orbital of the excess electron when projected onto the electron-localized Ti basis functions within SZV, DZV, DZVP. Note that all orbitals are defined within a +/- sign (phase). A phase difference can be seen for SZV and DZV. For DZVP, the contributing atomic function is now a d function, in contrast to the p function for SZV and DZV	53
Figure 3-6. Wavefunction plots of the moa orbitals in charged state: (1) Excess electron alpha-orbital #4 on the electron-localized Fe atom. (2) Beta orbital #9 on bridging oxygen atoms that facilitates superexchange. It shows a node on both oxygens implying the diffuse p-orbitals are out-of-phase between the compact p-orbitals.	58
Figure 3-7. MOA orbitals for all orbitals projection onto Fe and bridging oxygen bases.(1) For the excess electron in orb #4 of beta orbs in Fe. (2) Highest occupation number unoccupied orbital having a bigger difference with neutral state.	62
Figure 3-8. Plot of wavefunction when only the excess electron orbital is projected onto the basis functions of Vanadium and its surrounding oxygen quartet.	66
Figure 4-1. Bond increments and decrements in angstroms around titanium atoms in bulk rutile TiO_2 when an excess electron is localized on the left and right metal atoms in state 0 and state 1 respectively.	72
** *	



Figure 4-2. Collective variable definition	. 73
Figure 4-3 Graph showing how umbrella sampling energy function from equation 4.6 would allow a smoother transition at the crossing point	. 75
Figure 4-4 Schematic of the metadynamics along with an umbrella sampling function (in green) for smooth transition near the crossing point region, and quadratic walls on both sides to constrain the dynamics to region of interest.	. 76
Figure 4-5 Energy convergence in an equilibration run of 2.5 picoseconds.	. 77
Figure 4-6 a, b.) Free energy surface of a 16.4 picoseconds trajectory with a poor choice of the parameters gaussian width $\delta s=0.1$, height $w=0.007 \ eV$, deposition rate $\tau_G=100$. Two symmetric basins are formed as seen in the contour with a barrier of 0.05 eV. c.) A flip in the bond lengths observed during a hop at around 8.7 ps.	. 79
Figure 4-7 a,b.) Free energy surface of a 11 picoseconds trajectory with the parameters gaussian width $\delta s=0.05$, height $w=0.014 \ eV$, deposition rate $\tau_G=100$. Two basins are formed, where one seems to have a minimum near the ground state minimum and the other is approaching towards it. A barrier of 0.13 eV is observed, there is still a bit of dragging down near the transition region. c.) Two hops are observed during the run at around 1 and 7.7 ps. d.) corresponding bond length changes reflecting the hops are shown here.	. 81
Figure 5-1. Marcus diagram for two different systems with different electron transfer modes resulting in changed activation barriers	. 83
Figure 5-2. Time evolution of vibrational spectrum of electron-localized TiO2 obtained from Compressed sensing (left column, blue) compared with Fourier transform (right column, green) of the velocity autocorrelation function from an MD trajectory within NVT ensemble at 300K temperature.	. 88
Figure 5-3 Error in intensities at different times with respect to 4ps spectrum respectively for CS and FFT. Here $\delta I = I(t) - I(t=4 \text{ ps})$ on the y-axis	. 90
Figure 5-4. Vibrational spectrum of electron-localized TiO2 obtained from the Compressed sensing of velocity autocorrelation function of MD trajectory within NVT ensemble at 300K temperature. Phonon spectrum in red is obtained by small displacement method at T=0 K using phonopy. ¹ Shifts in frequencies with MD trajectory are observed when compared to phonopy output because of anharmonicity due to temperature.	. 91
Figure 5-5 Phonon spectra of subset of atoms that form two octahedrons, first of which is an electron-localized Ti atom and the six oxygen atoms surrounding it, second octahedron is a faraway Ti atom and surrounding six oxygen atoms that represent the bulk.	. 92
Figure 5-6 Phonon spectra of Ti-O stretches that form two octahedrons; first of which is an electron-localized Ti atom and the six Ti-O bonds surrounding it; second octahedron is a faraway Ti atom and surrounding six Ti-O bonds that represent the bulk.	. 93



Figure 5-7 Octahedrons of Ti and surrounding oxygen atoms in a TiO2 lattice. Ti atoms are in grey color and Oxygens are in red
Figure 5-8. Phonon spectra of Ti-O bond stretches in two octahedrons combined, which makes it a total of 12 bonds; six Ti-O bonds around the Ti that has an excess electron localized and the others are around the neighbor Ti atom
Figure 5-9 Phonon spectra of two octahedrons combined which makes it a subset of 12 atoms ; two of which are Ti atoms involved in electron transfer, one Ti has an electron localized and the other is its neighbor; and the surrounding 10 oxygens, two of which are bridging the Ti atoms
Figure 6-1 BMX ₃ compounds in distorted perovskite structure, where B=Ba, M=Ti/Zr/Hf, and X=O/S/Se
Figure 6-2 Bandgaps of BMX ₃ set of compounds
Figure 6-3 Electron polaron transfer barriers in BMX ₃ set of compounds
Figure 6-4 Hole polaron transfer barriers in BMX ₃ set of compounds
Figure 6-5 Training set of electron transfer barriers collected from literature as well as calculated by us
Figure 6-6 Predicted values versus the true values for random forests and gradient boosting models of regression
Figure 6-7 Feature importance for the selected 10 descriptors from random forests and gradient boosting models
Figure 6-8 Distribution of elements in the input data for prediction. Estimation of ET barriers are between the element B and its neighbor in ABX ₃
Figure 6-9 Estimations of activation barriers based on current model and top 100 compounds with lower barriers and potential good conductors
Figure 6-10 Elements in B Vs. A, and B Vs. X in ABX ₃ and their predicted electron transfer barriers in eV
Figure 7-1. (a) Structural model of covellite CuS. Potential ORR surfaces: (b) (110) planes with mixed Cu1 and Cu2 atoms, (c) Cu2 terminated and (d) Cu1 terminated (001) planes. The arrows indicate cleavage planes that produce the two different (001) surfaces

Figure 7-2 Optimized surface structures for intermediates in the ORR reaction and DFT study on different CuS surfaces. (a) O₂ adsorbed on the Cu1 terminated (001) surface, forming a peroxo bridge between two Cu atoms. (b) Dangling O₂ bound to the Cu2 terminated (001) surface. (c) Dangling O₂ bound to a Cu1 atom on the (110) surface with the



Cu atom bound to two sulfur atoms. (d) Dangling O ₂ bound to the Cu2 atom on the (110)	
surface with the Cu atom bound to three sulfur atoms	117

Figure 7-3 Reaction free energy diagrams for Cu1 terminated (001) surfaces (red), Cu2	
terminated (001) surfaces (blue), and (110) surfaces (green). Both bridge-like and dangling	
O ₂ adsorption mechanisms were applied to each CuS surface, and the stable surfaces are	
presented after surface relaxation. The oxygen adsorption energy on (110) surfaces was	
calculated separately on both Cu1 and Cu2 atoms.	119



Chapter 1 Introduction

1.1 Materials Genome Initiative

The Materials Genome Initiative (MGI), launched in 2011 by the US government² has been a tremendous catalyst for accelerating materials research in a wide array of fields, bringing together various federal agencies involved in the pursuit of material design and discovery. Materials design related to national security, human health, clean energy systems, infrastructure, and consumer goods are key areas of focus.



Figure 1-1. US government infographic on Materials Genome Initiative (MGI) from policy website (url: <u>www.mgi.gov</u>).

Broad strategic goals defined in the initiative³ are:

- a. to accelerate the pace of materials development and reduce time from conception to market
- b. to integrate experiments, computation, and theory with data-driven approaches



c. to facilitate access to materials data

d. to train the next-generation materials workforce

MGI has been quite successful in building a research infrastructure in the form of several interdisciplinary thematic research centers, software tools, materials databases, etc., reminiscent of the industrial revolution. There are several success stories in various domains such as functional materials, multicomponent materials for additive manufacturing, materials for information technologies, materials for health and consumer applications, and materials for clean energy.⁴

On the theory and computation side, the evolution of modern machines and big data analytics has contributed in generating large amounts of data from atomistic calculations, as well as deriving novel insights from the data. Transition to exascale computing, with new scalable software developments, is enabling researchers to leverage multiscale modeling and high throughput screening. MGI has a global impact and has led the way in inspiring other funding agencies all over the world to identify and support critical computing infrastructure in materials design. One realization of those efforts is a list of well-maintained materials databases ⁵⁻¹² across the world making research data accessible to the community at large:

- a. AFLOW distributed materials property repository
- b. Harvard Clean Energy Project Database
- c. Materials Cloud
- d. Materials Project
- e. NoMaD (Novel Materials Discovery) Repository
- f. Open Quantum Materials Database
- g. Computational Materials Repository



h. The Catalyst Genome

These databases are helping screen materials with desired properties, and inferences drawn by machine learning models from these huge datasets have guided experimentation.

1.2 Climate Change and MGI

Climate change is one of the major challenges of our time and MGI's emphasis has been on assisting to achieve real solutions. The rise in global temperatures due to human factors has increased the frequency of severe weather events viz. wildfires, droughts, coral bleaching, floods, and hurricanes. These events have put a heavy burden on countries' economies, quality of life, and their energy infrastructure. A major source of global warming is carbon dioxide emitted from fossil fuel consumption, whether it is coal for power generation, or gasoline for transportation, or burning of natural gas.

Due to worker health issues, increasing operating costs, and environmental concerns, coal-fired power generation is declining rapidly. For motor gasoline or aircraft fuel, steady increase in the number-of-miles-traveled across all transportation modes is a huge matter of concern. Although advancements are being made by raising the fuel economy standards to reduce the impact on the environment, the continued growth in travel demand outpaces these innovations. Emergence of electric vehicles is expected to offset some of these effects. Yet, the rising energy demands and the dire need to replace inefficient and limited fossil sources of energy require the ability to use renewable energy sources such as solar, wind, geothermal, bioenergy and nuclear in energy consumption.



Among renewable fuels, solar energy is the most abundant energy resource available to earth. Around 173,000 terawatts of solar energy strikes the earth continuously, which is 10,000 times more than the world's total energy use.¹³ Almost 42% of the solar radiation is made up of visible spectrum as seen in Figure 1-2. If we can capture and utilize this energy we can create a sustainable world for everyone.



Figure 1-2. The American Society for Testing and Materials (ASTM) G-173 spectra represent terrestrial solar spectral irradiance on a surface of specified orientation under US standard atmosphere. Major portion of solar radiation is in visible range of 400-700 nm, shaded in rainbow color.

1.3 Materials for Green Energy and Catalysis

Solar energy conversion via photo-electro-catalysis (PEC) or photovoltaics (PV) for power

generation involve charge carriers (electrons and holes) created by solar light absorption and that



diffuse through the light harvesting material. Favorable materials for such devices should exhibit the following features:

- strong absorption and carrier generation in the visible range of solar spectrum
- efficient carrier transport
- high redox reactivity (for photocatalysts)
- low cost and abundant availability

Materials based on inexpensive and abundant transition metals have great potential to fulfill these requirements. But, the wide range of structures and electronic properties among these materials require atomistic level investigations to understand their properties, their limitations, and, ultimately, to discover materials with enhanced characteristics, although experimental measurements will continue to be needed and essential.

1.4 Purpose of the study and methodology

My research work has been focused on determination of carrier mobility in crystalline systems and finding correlations with the chemical structure, composition, and environment. My work involved developing novel tools and approaches to characterize system for conversion of solar energy to chemical energy in crystalline systems in general.

Overall, my research dealt with the computation of charge carrier (electron and hole polarons) mobility within the framework of Marcus-Holstein theory of polaron transport, whereby a two-state model of charge transfer leads to an activation barrier for the polaron hops, as depicted in Figure 1-3. Tracing the geometry changes between the localized states gives a good prediction of the actual barrier. Thus, estimating these atomistic parameters gives us the macroscopic conductivity, we can see here the connection to atomistic hopping kinetics

$$I = \sigma V \qquad \sigma = q \rho_c \mu$$

Here, *I* is the current, σ is conductivity, *V* is voltage, *q* is the charge on the carrier, ρ_c is charge carrier concentration, μ is the mobility of carrier.



Figure 1-3. A simple diagram depicting Marcus electron transfer pathway between states A and B, wherein an activation barrier E_a and electronic coupling matrix element V_{AB} are labeled.

From classical kinetic theory charge carrier mobility is connected to diffusion coefficient D and thermal energy k_BT through Einstein-Smoluchowski equation,

$$\mu = \frac{qD}{k_B T} \qquad D = R^2 n k_{ET}$$

In the diffusion term the kinetic rate of transfer appears as,

$$k_{ET} = A * exp\left[\frac{-\Delta G^*}{\mathbf{k}_B T}\right]$$

where, pre-factor A depends on transmission probability κ , ΔG^* is the activation barrier that contains a quantity called reorganization energy λ , and the electronic coupling V_{AB} . We begin with the characterization of electron transfer in periodic solid-state systems from ab initio calculations and how these kinetic rates are obtained.

In chapter 2, we show a new implementation for calculation of the electronic coupling transition element V_{AB} in CP2K, a widely used ab initio package in materials research community. This development opens the full characterization of electron transfer in solid state. The approach is valid for any single-determinant wavefunction with localized character



representing the electronic structure of the system, from Hartree-Fock (HF) theory, to density functional theory (DFT), hybrid DFT theory, DFT+U theory, and constrained DFT (cDFT) theory. The implementation in CP2K reuses the high-performance functions of the code. The computational cost is equivalent to only one iteration of an HF calculation. We present test calculations for electron transfer in several systems, including a 1D-model of ferric oxide, hematite Fe₂O₃, rutile TiO₂, and finally bismuth vanadate BiVO₄.

In chapter 3, we show qualitative analysis of coupling and superexchange involved in charge transfer without explicit calculation. We show a new periodic implementation for wavefunction characterization based on Maximal Orbital Analysis (MOA), in CP2K. MOA is a variant of population analysis methods whereby for a wavefunction, the method defines the maximal projection of the wavefunction onto a subgroup of atoms. This helps in rudimentary characterization of super-exchange interactions in ET. How much of the tail of a localized-state wavefunction spreads onto linker bridge fragments defines the extent of coupling and can be ascertained with fragment-wise projections. Both the MOA and V_{AB} implementations include the efficient application of corresponding orbitals transformation (COT). ¹⁴

In chapter 4, we look at the direct estimation of activation barriers from molecular dynamics simulations. Application of Ab Initio Molecular dynamics has the potential to remove assumptions involved in the Marcus-Holstein charge transfer model about the linear pathway. The only bottleneck in this process is the polaron hopping process, which is a rare-event and occurs at a timescale almost 10⁵ times longer than the atomic vibrations, thus requiring lengthy trajectories and huge computational efforts. Polaron hopping events are associated with concerted increase and decrease in bonds around the charge localized metal atom and its neighbor. Metadynamics is an enhanced sampling method which allows us to use this



www.manaraa.com

characteristic by defining a reduced variable space and propagating the trajectory in it, thus sampling highly relevant areas of the potential energy surface. We used a variant of metadynamics combined with umbrella sampling to explore the potential energy surface. The challenge here is in defining an efficient collective variable that truly represents the physics of the transfer process. Faster sampling of configuration space with bias and reconstructing free energy surface by removing the bias would give us the activation barrier for electron transfer.

In chapter 5, we look at an alternate way of estimating the activation barrier from molecular dynamics. Instead of free energy surface we try to obtain the breathing mode, the vibration mode involved in bond stretches and compressions around the charge localized site and its neighbor, so that we can estimate the activation barrier. Traditionally, post-processing of MD data via Fourier transform of velocity autocorrelation function gives us the vibrational spectrum. If we isolate the vibrations associated with the specific set of atoms that are involved in a transfer pathway we can find the dominant mode to be the breathing mode. As mentioned before polaron hopping is a rare-event and we do need very lengthy trajectory for better resolution of peaks in the spectrum. Alternatively, a sparse-signal reconstruction method, called compressed sensing, is found to be better than Fourier transform in generating a better resolved vibration spectrum in molecules with very short trajectories. ¹⁵

In chapter 6, we derive which chemical descriptors correlate well with conductivity based on a dataset of polaron transfer barriers. Current screening pipelines for solar energy conversion materials either ignore carrier transport completely or include simplified models viz., effective masses of charge carriers. ^{16, 17} Electron or hole effective masse theories are usually calculated from a short range of Brillouin zone, but do not capture the effects of whole band structure. Additionally, electron-phonon interactions and phonon-induced trappings or re-excitations in



transition metal compounds limit the effective mass approach. To estimate the conductivity from effective mass we would need to have the relaxation time of the carriers, which is often assumed to be constant in a high throughput study because of the computational complexity. Any insights based on this model might be highly sensitive to the level of theory, in particular for the DFT+U theory and specifically the U_{eff} value used in that theory. To overcome some of these approximations we use the linear approximation of the Marcus curve as illustrated by Dupuis, et al., ¹⁸, and is proved to give a good estimate of conductivity in realistic systems.

In chapter 7, we go beyond the theory and modeling of carrier transport and highlight an investigation of chemical reactivity at the surface of materials. Specifically, we show the thermodynamic pathways for a photocatalyst, Covellite, in water splitting reaction from ab initio calculations. Covellite is one of the dominant copper sulfide minerals with the stoichiometric formula CuS. Our experimental collaborators prepared monodispersed hexagonal covellite (CuS) nanoplatelets (NPIs) and tested the electrochemical activity for the oxygen reduction reaction (ORR) in alkaline solution. Size- and shape-dependent electrochemical activity of nanostructures reveals relationships between nanostructure design and electrochemical performance. We validated the findings of facet selectivity with density functional theory calculations which show anisotropy of conductivity and electrochemical activity. The lowest computed oxygen adsorption energy was on Cu sites exposed by cleaving covellite along (001) planes through tetrahedrally-coordinated Cu atoms. These CuS NPI-carbon Nano catalysts provide inspiration for creating well-controlled layered nanomaterials for electrochemical applications and open opportunities to design new electrocatalysts using transition metal sulfides.



Having introduced the core parts of my thesis going forward we will see in greater detail the work done in each of the areas. We will start with the estimation of Marcus parameters for periodic solids in chapter 2.



Chapter 2 Electronic coupling calculation in periodic systems

2.1 Introduction

The theory of electron transfer (ET) in gas and solution phases has a very long history, dating back to the work of Hush and collaborators¹⁹ and Marcus and collaborators.²⁰⁻²⁶ Fundamentals of the Marcus model have been investigated in numerous computer simulations of redox reactions in solution²⁷⁻³⁶ with a focus on the characterization of the free energy surface, and dealing much less with the electronic coupling. A number of reviews are also available about electron transfer investigated by computation and simulation in biochemistry.³⁷⁻⁴⁰ Modeling of charge transport in the solid state (polarons) has also a long history, with the seminal work of Friedman and Holstein⁴¹, Emin and Holstein^{42, 43}, Austin and Mott⁴⁴, and Emin⁴⁵⁻⁴⁸ for example, and DFT calculations reported in recent years.⁴⁹⁻⁵² At the intersection of the solid state and chemistry, the structure and transport of charge carriers in conducting polymers have been at the forefront of research for many years.⁵³⁻⁶¹ Indeed the experimental work spurred a great deal of theoretical efforts toward the characterization of carriers by Su, Schrieffer, and Heeger^{62, 63} with extensions by Bredas and collaborators in many areas of organics, including organic photovoltaics.⁶⁴⁻⁷¹ Beyond these studies recent years have seen a growing interest in obtaining molecular-level details of redox chemistry at oxide surfaces in electrolyte environments.^{49, 72-81} Lastly, the recent push for renewable energy and efficient solar-to-electricity and solar-to-fuel conversion materials, has greatly increased the interest in understanding and manipulating carrier transport in inorganic semi-conductors. ^{50, 82-90} Several of these studies showed already that polaron diffusion mobility extracted from Einstein diffusion model and DFT-derived ET rates can be within one order of magnitude of experimental values^{49, 50, 82} with energy barriers within ~



0.05 eV from experimental values. We refer the reader to the papers and reviews referenced above to experience the breadth of applications involving ET computation and simulation.

The work described in this chapter deals with a technical development that enables ET computation in all these domains, although the driving force for our research has been the computation of electron transfer in the solid state. A growing number of studies have appeared about carrier transport in the literature, most focusing on energetics parameters such as stability and reorganization energy (in Marcus/Holstein parlance). They often leave out the electronic coupling V_{AB} that, however, plays a key role as a descriptor of the diabatic or adiabatic nature of ET as well as enters the rate expression. In a limited number of these studies, Dupuis and co-workers^{18, 91-93} resorted to cluster models to evaluate the electronic coupling. The present work overcomes this shortcoming.

Theoretical studies of ET with *n*-electron wavefunctions started with Newton and collaborators using localized quasi-diabatic (non-orthogonal) states. ^{31-33, 94, 95} Various approaches to calculating the electronic coupling element were developed⁹⁶⁻⁹⁹ and several molecular implementations have been available for some time.^{100, 101} Many studies using semi-empirical or *ab initio* Hartree-Fock (HF) theories have been reported.¹⁰²⁻¹⁰⁴ With the advent of density functional theory^{105, 106} (DFT) and the development of the constrained DFT method (*cDFT*), the interest has shifted to ET described with DFT and cDFT,¹⁰⁷⁻¹¹² both for molecules and organic solids. ^{52, 113-120} Different approaches are used to 'localize' the initial and final states of ET, including charge- or spin-constrained DFT or fragment-based localization. For a recent review, see the work of Oberhofer *et al.*⁵²

In the present research, our starting point for localized quasi-diabatic non-orthogonal nelectron states are molecular or periodic DFT Kohn-Sham wavefunctions with correction for



self-interaction error (hybrid functional DFT ^{121, 122} or DFT+U ^{123, 124}). Like with HF theory, they offer a means to obtain localized states without external constraints. Note that our formalism is not limited by this 'requirement' and can treat *cDFT* or fragment-projected states as well. We aim to calculate the electronic coupling matrix element for any type of quasi-diabatic *DFT*-based states in molecular or periodic DFT calculations.



Figure 2-1. Spin density of an electron polaron localized on a Ti site in TiO2. We aim to calculate the rate for the polaron to hop between two Ti sites. The blue spheres are polaronic Ti atoms, the red spheres are O atoms, and the silver spheres are Ti atoms.

The present implementation involves a slightly simplified form of the Farazdel formulation¹⁰¹ for spin-unrestricted *HF* wavefunctions, using the corresponding orbitals transformation.¹²⁵ The present work goes beyond the recent work of Bylaska and Rosso¹²⁶ in that we can treat periodic *DFT*-based wavefunctions, including *hybrid* functional wavefunctions for molecules and periodic solids, *DFT+U* wavefunctions, and *cDFT* wavefunctions, that are popular in the solid state community. We note that, beyond the issue of the often-prohibitive cost of periodic *HF* calculations, the use of *HF* theory is problematic as it does not account for strong correlation effects existing, for example, in semiconductors.



The chapter is organized as follows: in section 2.2, we present the equations for the electronic coupling element valid in a molecular case and in a periodic case. We give details of the implementation in the CP2K code that uses Gaussian-type basis functions as the expansion set of the one-electron Kohn-Sham (KS) states. In section 2.3 we present and discuss results for several benchmark systems, including hole transfer in He₂⁺ and Zn₂⁺, electron polaron transfer in a 1D chain of OH-bridged Fe^{III} ions, in bulk rutile TiO₂, and in bulk hematite Fe₂O₃, and lastly in bismuth vanadate BiVO₄. In section 2.2.1, we elaborate on our choice of the exact *n*-electron Hamiltonian for the calculation of V_{AB} as it removes a theoretical ambiguity. In section 2.2.2, we give essential details of the code implementation.

2.2 Formulation and Implementation

For an excellent review of electron transfer theory, we refer the reader to the recent paper by Bylaska and Rosso. ¹²⁶ An electron polaron transfer in an inorganic solid is depicted in Figure 2-1 (here TiO₂). We are interested in the rate of transfer (hopping) of the electron (polaron) from one Ti site to another. The localization of the excess electron density induces a lattice relaxation around the localization site. When the lattice relaxation is limited to the region near the localization site, we have what is known a small polaron.⁴³ Small polaron transport is prevalent in inorganic and organic semi-conductors.^{65, 127} In the two regimes of diabatic and adiabatic transfer, the hop involves a 'transfer' of the lattice distortion from one site to the other. Just like for molecules, the system can be looked at as a double-well potential, the electron hops back and forth from one well to the next at some characteristic frequency which depends on the height of the potential barrier.





Figure 2-2. Schematic of the two-well potential energy surface associated with electron or hole transfer in molecules and in the solid state (reproduced from Farazdel et al. [71]). The solid curves are the adiabatic surfaces; the dashed lines depict the diabatic states. Q_A and Q_B are the equilibrium coordinates of the A state and B state, and Q_c represent the coordinates of the lowest energy structure on the crossing seam of the diabatic surfaces. λ is the reorganization energy, $|\Delta E|$ is the exothermicity of the electron transfer, E_d is the diabatic activation energy, E_a is the adiabatic activation energy, and V_{AB} is the electronic coupling between states A and B.

A schematic representation of the potential energy surface (PES) of the system as a function of the nuclear coordinates Q is shown in Figure 2-2. The initial state A with the left-localized electronic state Ψ_A resides in a local minimum on the PES that corresponds to its equilibrium nuclear configuration Q_A . The final state B with its right-localized electronic state Ψ_B resides similarly in a local minimum on the PES denoted Q_B . The two minima may differ in energy, and the exothermicity is denoted ΔE .

The quantity V_{AB} shown in Figure 2-2 plays a key role in ET or polaron transfer theory. It is related to the "electronic coupling" $H_{AB} = \langle \Psi_A | H | \Psi_B \rangle$ between states *A* and *B*, where *H* is the total *n*-electron Hamiltonian (excluding the nuclear kinetic energy and nuclear repulsion terms). When $H_{AB} = 0$, the two (diabatic) surfaces *A* and *B* intersect at a crossing seam where the



للاستشارات

states have the same energy and the same nuclear configuration. The ET is then a diabatic transition governed by the Franck-Condon principle with conservation of energy. When $H_{AB} \neq 0$, the states Ψ_A and Ψ_B do not diagonalize the electronic Hamiltonian H and the degeneracy of the states is removed. We have an avoided crossing; the two surfaces are now adiabatic surfaces for *n*-electron states Ψ_+ and Ψ_- with energies E_+ (upper state) and E_- (lower state) extracted from the 2×2 secular equation arising from writing the wavefunction of the system as a linear combination of the two quasi-diabatic states Ψ_A and Ψ_B in the framework of the two-state model:

$$\Psi_{+}(Q) = c_{+}^{A}(Q)\Psi_{A}(Q) + c_{+}^{B}(Q)\Psi_{B}(Q)$$

$$\Psi_{-}(Q) = c_{-}^{A}(Q)\Psi_{A}(Q) + c_{-}^{B}(Q)\Psi_{B}(Q)$$

$$H(Q)C_{\pm}(Q) = E_{\pm}(Q)S(Q)C_{\pm}(Q)$$

$$C_{\pm}(Q) = \begin{pmatrix} c_{\pm}^{A}(Q) \\ c_{\pm}^{B}(Q) \end{pmatrix}$$

$$H(Q) = \begin{pmatrix} H_{AA}(Q) & H_{AB}(Q) \\ H_{AB}(Q) & H_{BB}(Q) \end{pmatrix}$$

$$S(Q) = \begin{pmatrix} S_{AA}(Q) & S_{AB}(Q) \\ S_{AB}(Q) & S_{BB}(Q) \end{pmatrix}$$
(2.1)

with

$$H_{AA}(Q) = \langle \Psi_{A}(Q) | H(Q) | \Psi_{A}(Q) \rangle$$

$$H_{BB}(Q) = \langle \Psi_{B}(Q) | H(Q) | \Psi_{B}(Q) \rangle$$

$$H_{AB}(Q) = \langle \Psi_{A}(Q) | H(Q) | \Psi_{B}(Q) \rangle$$

$$S_{AA}(Q) = \langle \Psi_{A}(Q) | \Psi_{A}(Q) \rangle = 1$$

$$S_{BB}(Q) = \langle \Psi_{B}(Q) | \Psi_{B}(Q) \rangle = 1$$

$$S_{AB}(Q) = \langle \Psi_{A}(Q) | \Psi_{B}(Q) \rangle$$
(2.1)

The secular equation has the form:



$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0$$

$$(2.2)$$

The separation between the adiabatic surfaces is given by:

$$\Delta(Q) = E_{+} - E_{-} = \frac{2}{(1 - S_{AB}^{2})} \left\{ \frac{1}{4} (H_{AA} - H_{BB})^{2} - (H_{AA} + H_{BB}) H_{AB} S_{AB} + H_{AB} S_{AB}^{2} + H_{AB}^{2} \right\}^{\frac{1}{2}}$$
(2.3)

and by convention

$$V_{AB} = \frac{1}{2}\Delta(Q = Q_C) = \frac{1}{(1 - S_{AB}^2)} \left\{ H_{AB} - \frac{S_{AB}(H_{AA} + H_{BB})}{2} \right\}$$
(2.4)

 V_{AB} is a key quantity that appears in classical²¹, semi-classical¹²⁸, and quantum mechanical^{129, 130} treatment of ET theory. The rate expression that ensues in the diabatic regime is ¹³¹:

$$k_{ET} = \frac{2\pi}{\hbar} V_{AB}^2 \frac{1}{(4\pi\lambda k_B T)^{\frac{1}{2}}} \exp\left(\frac{-[\lambda + \Delta E]^2}{4\lambda k_B T}\right)$$
(2.5)

and in the adiabatic case⁴⁹ it is:

$$k_{ET} = i\nu_n exp\left(\frac{-E_a}{k_B T}\right)$$
$$E_a = -\frac{\lambda}{4} + \frac{(\lambda^2 + 4V_{AB}^2)^{\frac{1}{2}}}{2} - V_{AB}$$
(2.6)

In both cases the rate can be determined from the knowledge of λ and V_{AB} . In the present work we use Kohn-Sham states to determine the quasi-diabatic states and we use the exact *n*-electron Hamiltonian to determine the state mixing and their interactions. Important theoretical considerations governing these choices are expounded upon in greater detail below.

2.2.1 Considerations about localized states and VAB calculations

The essential differences between several formalisms and implementations of ET lie the quasi-diabatic *n*-electron states Ψ_A and Ψ_B and in the expression used for the evaluation of the


Hamiltonian elements H_{AA} , H_{BB} , and H_{AB} . In the recent of work of Bylaska and Rosso¹²⁶ valid for molecular and periodic calculations, Ψ_A and Ψ_B are *HF* states, and *H* is the total *n*-electron Hamiltonian, the evaluation of which introduces exact exchange terms requiring exact exchange integrals as in *HF* theory. In the work of Van Voorhis and collaborators ¹⁰⁹ using *cDFT*, the Ψ_A and Ψ_B *n*-electron states are Kohn-Sham-like states for which constraints have been applied to enable charge or spin localization, and the Hamiltonian terms in eq.(1) are taken as the *DFT* Kohn-Sham Hamiltonian. Strictly speaking, the *DFT* Hamiltonian for *A* is not the same as the Hamiltonian for *B* since the *DFT* Hamiltonian is state-specific through the functional of the density. As such the KS Hamiltonian depends on the electron density of state *A* or *B* respectively, albeit it is the case that $E_A^{KS} \equiv E_B^{KS}$ when the ET process is thermo-neutral. If we denote H(1,2,...,n) the total *n*-electron Hamiltonian operator, and $H_A(1,2,...,n)$ and $H_B(1,2,...,n)$ the Kohn-Sham operators for state *A* and state *B* respectively, it follows that:

$$H_{A}(1,2,...,n) \neq H(1,2,...,n)$$

$$H_{B}(1,2,...,n) \neq H(1,2,...,n)$$

$$E_{A}^{KS} = \langle \Psi_{A}^{KS} | H_{A}(1,2,...,n) | \Psi_{A}^{KS} \rangle \neq \langle \Psi_{A}^{KS} | H(1,2,...,n) | \Psi_{A}^{KS} \rangle$$

$$E_{A}^{KS} = \langle \Psi_{B}^{KS} | H_{B}(1,2,...,n) | \Psi_{B}^{KS} \rangle \neq \langle \Psi_{B}^{KS} | H(1,2,...,n) | \Psi_{B}^{KS} \rangle$$
(2.7)

We can project the occupied Kohn-Sham (KS) *1*-electron states onto the Hartree-Fock *1*-electron states (occupied and unoccupied):

$$(\varphi_{1}^{KS,A}, \varphi_{2}^{KS,A}, ..., \varphi_{n}^{KS,A}) = (\varphi_{1}^{HF}, \varphi_{2}^{HF}, ..., \varphi_{n}^{HF}) \times C_{(M,n)}^{A}$$

$$(\varphi_{1}^{KS,B}, \varphi_{2}^{KS,B}, ..., \varphi_{n}^{KS,B}) = (\varphi_{1}^{HF}, \varphi_{2}^{HF}, ..., \varphi_{n}^{HF}) \times C_{(M,n)}^{B}$$

$$(2.8)$$



where the *C*'s are $M \times n$ matrices, *M* is the total number of *1*-electron *HF* states, and *n* is the number of *1*-electron occupied *KS* states. It follows that we can expand the *KS* determinant as a linear combination of excited *HF* determinants, following Lowdin¹³²:

$$\Psi^{KS} = c_0 \Psi^{HF} + \sum_{i}^{a} c_{i \to a} \Psi^{HF}_{i \to a} + \sum_{i,j}^{a,b} c_{i,j \to a,b} \Psi^{HF}_{i,j \to a,b} + \sum_{i,j,k}^{a,b,c} c_{i,j,k \to a,b,c} \Psi^{HF}_{i,j,k \to a,b,c} + \cdots$$
(2.9)

In eq.(A.3) $\Psi_{i,a}^{HF}$, $\Psi_{i,j,a,b}^{HF}$, $\Psi_{i,j,k,a,b,c}^{HF}$, ... denote singly-, doubly-, triply-excited, ... determinants where occupied orbital *i*, *j*, *k*, ... have been replaced by unoccupied orbitals *a*, *b*, *c*, In effect we can expand the *KS* determinant as a configuration interaction (CI) expansion involving the *HF* determinant plus singly-excited determinants plus doubly-excited determinants plus ... *n*excited determinants.¹³² It emerges that a single determinant *KS* wavefunctions can be conceived as very compact representations of complex CI wavefunctions based on excited *HF* determinants. In our case, they have the desired character of representing 'localized' states, but in addition, they also capture a description of electron correlation that *HF* wavefunctions do not.

We can apply the variational principle to the two KS n-electron states using the total nelectron Hamiltonian to obtain the 'best' linear combination. This is what is expressed in eqs. (1 and 2).

$$\begin{split} \Psi_{\pm} &= c_{\pm}^{A} \Psi_{A}^{KS} + c_{\pm}^{B} \Psi_{B}^{KS} \\ H_{AA} &= \langle \Psi_{A}^{KS} | H(1, 2 \cdots n) | \Psi_{A}^{KS} \rangle \\ H_{BB} &= \langle \Psi_{B}^{KS} | H(1, 2 \cdots n) | \Psi_{B}^{KS} \rangle \\ H_{AB} &= \langle \Psi_{A}^{KS} | H(1, 2 \cdots n) | \Psi_{B}^{KS} \rangle \end{split}$$

$$(2.10)$$

The diagonal terms in the secular equation in eq. (2) of the main text are now the 'exact' energies associated with the KS determinants (using the exact *n*-electron Hamiltonian). The off-diagonal terms can be calculated through the usual formalism of the "corresponding orbital

transformation" (COT) that is a bi-orthogonalization procedure applicable to spin-polarized states as described below. Lastly, we note that Marcus/Holstein theory does not tell us how to build the quasi-diabatic states: we may use "localized" *HF* states, "localized" *DFT* states, "DFT+U" states, "hybrid *DFT*" states, or "constrained *DFT*" states. The formalism is applicable to molecular systems as well as periodic systems, and the computational cost for the calculation of *V*_{AB} is equivalent to one iteration of a *HF* calculation.

2.2.2 Energy calculation and contributing terms in CP2K

The difficulty in evaluating the interaction and overlap terms H_{AB} and S_{AB} between states A and B arises from the non-orthogonality of the (*1*-electron states) orbitals a and b. The corresponding orbital transformation (COT) of King *et al.*¹²⁵ defines a unitary transformation of the a orbitals of state A and another one for the b orbitals of state B that make the transformed orbitals mutually orthogonal between states A and B, thus facilitating the calculation of S_{AB} and H_{AB} :

$$a = |\mu\rangle A$$

$$b = |\mu\rangle B$$

$$D = A^{\dagger} \langle \mu | \mu \rangle B$$

$$\hat{a} = aV = |\mu\rangle \hat{A}$$

$$\hat{b} = bU = |\mu\rangle \hat{B}$$

$$D = \langle a | b \rangle$$

$$\hat{d} = \langle \hat{a} | \hat{b} \rangle = U^{\dagger} DV$$
(2.11)



In eq.(2.11), $|\mu\rangle$ denotes the one-electron basis set used in the expansion of the *1*-electron states *a* and *b*. We obtain a generalized density matrix *P* from the transformed orbitals that enables the calculation of *1*- and *2*-electron contributions to the Hamiltonian matrix element *H*_{AB}:

$$P = \hat{A}T\hat{B}$$

$$\Omega_{AB}^{(1)} = (detU)(detV^{\dagger}) \sum_{\mu\nu}^{M} P_{\mu\nu} \omega_{\mu\nu}^{(1)}$$
$$\omega_{\mu\nu}^{(1)} = \langle \chi_{\mu} | \omega^{(1)} | \chi_{\nu} \rangle$$
$$T_{ii} = \prod_{j \neq i}^{N} \hat{d}_{jj}$$
$$prod = \prod_{k=1}^{N} \hat{d}_{kk}$$
$$\Omega_{AB}^{(2)} = \frac{1}{2} (detU)(detV^{\dagger})(prod)^{-1} \sum_{\mu\nu\lambda\sigma}^{M} P_{\mu\nu} P_{\lambda\sigma} \{ \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\sigma | \lambda\nu \rangle \}$$
(2.12)

We note that the generalized density matrix P is not symmetric due to the differently localized states A and B. To take advantage of existing functionalities in CP2K that are extensively tuned for massively parallel processing, we have found it convenient to decompose P into a symmetric matrix and an anti-symmetric matrix:

$$P = P_{sym} + P_{anti}$$

$$P_{sym} = \frac{P + P^{\dagger}}{2}$$

$$P_{anti} = \frac{P - P^{\dagger}}{2}$$
(2.13)

Here, we gather for convenience the essential equations embodied in CP2K that are relevant to the calculation of V_{AB} developed here. CP2K implements a mixed Gaussian and plane wave



www.manaraa.com

method to perform efficient *ab initio* calculations.¹³³⁻¹⁴² CP2K is highly parallel and scales linearly with the system size even for condensed phase systems. The essential feature of the Gaussian and plane wave approach is the dual representation of the electron density that allows an efficient treatment of electrostatics. We implemented our calculation of V_{AB} within the GAPW (Gaussian augmented plane wave) and GPW(Gaussian Plane Wave) formalisms of CP2K ^{134, 135} making use of many routines available in CP2K, ^{137, 138} in particular the Coulomb engine and the exchange engine. The re-use of subroutines was made possible because of the decomposition of the generalized density matrix in the V_{AB} calculation into a symmetric component and an anti-symmetric component.

The expression for the total energy of a molecular or crystalline system in the GPW^[136] formalism is as follows:

$$E_{Total} = E^{T}[n] + E^{V}[n] + E^{H}[n] + E^{X}[n] + E^{Ion-Ion}$$

$$= \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_{\mu}(\boldsymbol{r}) \left| -\frac{\Delta}{2} \right| \varphi_{\nu}(\boldsymbol{r}) \rangle$$

$$+ \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_{\mu}(\boldsymbol{r}) | V_{nl}^{PP}(\boldsymbol{r}, \boldsymbol{r}') | \varphi_{\nu}(\boldsymbol{r}) \rangle + \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_{\mu}(\boldsymbol{r}) | V_{loc}^{PP}(\boldsymbol{r}, \boldsymbol{r}') | \varphi_{\nu}(\boldsymbol{r}) \rangle \quad (2.14)$$

$$+ 4\pi \Omega \sum_{|\boldsymbol{G}| < G_{C}} \frac{\check{n}^{*}(\boldsymbol{G})\check{n}(\boldsymbol{G})}{\boldsymbol{G}^{2}} + E_{HFX} + \frac{1}{2} \sum_{I \neq J} \frac{Z_{I} - Z_{J}}{|\boldsymbol{R}_{I} - \boldsymbol{R}_{J}|}$$

where n denotes the electron density, T is the electronic kinetic energy, V is the electronic potential energy, H is the Hartree energy, X is the exchange energy (exchange correlation in case of DFT), and PP stands for pseudo-potential.

The use of pseudo-potentials is a well-established technique to represent the nuclei and core electrons. They have local and non-local parts. The long-range contribution to the local part of pseudo-potentials to the energy, the Hartree energy, and the ion-ion nuclear interaction energy



are grouped together as electrostatic interactions. They are treated via Ewald sum on a FFT grid. The short-range part of the local pseudopotentials is treated on a real grid.

$$E_{electrostatic} = \int V_{loc}^{PP}(r)n(r)dr + 4\pi\Omega \sum_{|G| < G_{C}} \frac{\check{n}^{*}(G)\check{n}(G)}{G^{2}} + \frac{1}{2}\sum_{I \neq J} \frac{Z_{I} - Z_{J}}{|R_{I} - R_{J}|}$$
(2.15)

For computational convenience a Gaussian core charge is introduced for each nucleus so that the above expression becomes:

$$E_{electrostatic} = \int V_{loc}^{SR}(r)n(r)dr + \frac{\Omega}{2} \sum_{G} \tilde{n}_{tot}^{*}(G) \frac{4\pi \tilde{n}_{tot}(G)}{G^{2}} + \frac{1}{2} \sum_{I \neq J} \frac{Z_{I}Z_{J}}{|R_{I} - R_{J}|} \operatorname{erfc} \left[\frac{|R_{I} - R_{J}|}{\sqrt{R_{I}^{c^{2}} + R_{J}^{c^{2}}}} \right] - \sum_{I} \frac{1}{\sqrt{2\pi}} \frac{Z_{I}^{2}}{R_{I}^{c}}$$
(2.16)

The last three terms are the total Hartree energy (E^{H}) , the 'nuclear overlap' energy (E^{ovrl}) , and the self-energy (E^{self}) . The electron density in GAPW is treated differently as compared to GPW. It is divided into three parts, a smooth global density distributed over the whole space, and two non-overlapping atom centered soft and hard densities. These densities are constructed such that, within the region around the atoms, the soft density cancels the all-inclusive smooth density, and in the interstitial regions, soft and hard densities cancel out.

$$n = \tilde{n} - \tilde{n}^{1} + n^{1}$$

$$n^{1} = \sum_{A} n^{1}_{A}$$

$$\tilde{n}^{1} = \sum_{A} \tilde{n}^{1}_{A}$$
(2.17)

where, n = electron density, $\tilde{n} =$ smooth global density, \tilde{n}^1 =atom-centered soft density, and n^1 =atom-centered hard density. More details on the construction of densities can be found in

المنارات

23

Lippert *et al.*^{134, 135} The Hartree energy term is computed in two parts, one with the smooth global density using a poisson solver on FFT grids, and the second part on an atomic Lebedev grid (spherical grid) with the atom-centered densities. Therefore

$$E_{H}[n+n^{Z}] = E_{H}[\tilde{n}+\tilde{n}^{0}] + \sum_{A} E_{H}[n^{1}_{A}+n^{Z}_{A}] + \sum_{A} E_{H}[\tilde{n}^{1}_{A}+n^{0}_{A}] + E_{H}[n^{0}] - E_{H}[\tilde{n}^{0}]$$
(2.18)
+ $\int d\mathbf{r} V_{H}[n^{0}-\tilde{n}^{0}]\tilde{n}$

where, the operators E_H and V_H are:

$$E_{H}[n] = \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \frac{n(\mathbf{r}) \, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
$$V_{H}[n](\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(2.19)

The *HF* Exchange energy calculation is calculated for the Γ -point only for periodic systems in CP2K, and makes use of a truncated coulomb operator using Gaussian basis sets. Implementation details can be found in papers by Guidon, et al.[^{137, 138, 143}]

$$E_x^{PBC} = -\frac{1}{2N_k} \sum_{i,j} \sum_{\mathbf{k},\mathbf{k}'} \iint \psi_i^{\mathbf{k}}(r_1) \psi_j^{\mathbf{k}'}(r_1) g(|r_1 - r_2|) \psi_i^{\mathbf{k}}(r_2) \psi_j^{\mathbf{k}'}(r_2) d^3r_1 d^3r_2 \qquad (2.20)$$

For the purpose of our V_{AB} calculation, we needed to separate H_{AB} into:

- 1. two-electron contributions coulomb (or Hartree) and exchange
- 2. one-electron contributions nuclear attraction and kinetic energy and
- 3. nuclear energy (ion-ion).

The three contributions to the energies (Coloumb, ion-ion, and nuclear attraction) were obtained by three successive calls to the Poisson solver, the first time providing the electron density only, the second time providing the nuclear density only, and the third time providing the total density.



	1	2	3
Energy contributions			nuc-elec, kinetic
Energy contributions	elec-elec	nuc-nuc	energy
Associated CP2K function calls	2e- energies	0e- energies	1e- energies
Exchange: hfx_ks_matrix()	symmetric and anti-symmetric parts	-	-
	call with electron-	call with	Regular call with
E_Hartree: pw_poisson_solve()	only density	nuclear-only	combined $(1+2)$
	yy	density	density
E Hartree 1centered:	call with electron-	call with	Regular call with
Vh 1c gg integrals()	only density	nuclear-only	combined $(1+2)$
· ···		density	density
Self-energy:	-	Analytical term	-
calculate_ecore_self()			
Potential energy:	_	_	from core
build_core_hamiltonian_matrix()			Hamiltonian
Kinetic energy:			from core
build_core_hamiltonian_matrix()	-	-	Hamiltonian
	Coulomb +	Ion-ion	Ion-electron
Summation by column gives:	Exchange	interaction	attraction
	energy	energy	energy

Table 2-1. Outline of one-electron, two-electron, and nuclear energy contributions obtained by splitting the subroutine calls within the 'quick-step' code and its construction of the Kohn-Sham matrix in CP2K.

Subtraction of the electron-only and nuclear-only energies, from the energy obtained with the combined density, yielded the one-electron contribution. We note that a part of the nuclear-only energy term cancels out a term in the pseudopotential contribution and hence the nuclear-only energy is equal to the pure nuclear energy only in cases of all-electron calculations. A similar procedure was applied to the one-center Hartree energy terms. The HFX routine provides the two-electron exchange energy. In the end the various energy contributions were gathered as shown in Table 2-1.

When using the GPW formalism, there are no 1-centered Hartree energy terms. GAPW

requires much care and tuning of parameters on a case-by-case basis, so that for periodic

المنسارات

25

calculations it may be preferable to use the GPW method. GAPW and GPW results come out to be the same for V_{AB} calculations. For all-electron calculations the GAPW method is necessary. Convergence with respect to the radial atomic grids and the FFT grid must be checked to get accurate values of V_{AB} .

For the calculation of V_{AB} , the COT method requires the orbitals of both initial and final states. For the sake of convenience, this is done in CP2K in a mixed energy calculation setup so that both states are available in the quick-step force environment at the same time. Generating the two localized states in itself require making use of broken symmetry section in CP2K, or Hubbard U, or constrained DFT, which are not discussed here. Using the generalized density matrix obtained from the initial and final state orbitals, a single step of *HF* energy calculation is carried out to obtain the segregated one-electron and two-electron contributions as shown in Table 2-1.

We make use of the partitioning of the generalized density matrix into a symmetric matrix and an anti-symmetric matrix. For the Coulomb and one-electron terms the symmetric part of the generalized density matrix suffices as the operators are symmetric. However, for the calculation of exchange energy, both parts are needed, and two 'exchange' calculations are carried out by passing symmetric and anti-symmetric matrices. The two contributions are summed up in the end. When using DFT-based states as initial and final states (non-HF orbitals) as input, then the theory developed above requires that we calculate the exact HF energy H_{AA} and H_{BB} (these quantities are already available if initial and final states are HF states). Finally, we assemble V_{AB} by multiplying the energy contributions with the appropriate pre-factors.



26

2.2.3 Implementation in CP2K

We adapted the implementation by Farazdel in HONDO¹⁴⁴ to the CP2K¹³³ program, which can deal with periodic calculations. A summary of the steps includes:

Obtain the molecular orbitals of both states, *A* and *B*, at a *DFT/HF/Hybrid-DFT/cDFT/DFT+U* level of theory in CP2K.

For both alpha and beta spins, do the following:

- I. Calculate the overlap matrix **D** from $\mathbf{D} = \mathbf{B}^{\dagger}\mathbf{S}\mathbf{A}$, where **A** and **B** are eigenvectors of the quasi-diabatic states obtained in step 1, and *S* is the overlap matrix over the atomic orbitals.
- II. Carry out the COT transformation (one for spin α , and one for spin β) by singular value decomposition of matrix **D**, where $\mathbf{d} = \mathbf{U}^{\dagger} \mathbf{D} \mathbf{V}$.
- III. U and V are unitary matrices and their determinants are equal to one. This can be an internal check during implementation.
- IV. Form the matrices \widehat{A} , \widehat{B} , T, and the generalized density matrix P.
- V. Compute the overlap as $S_{AB} = (\det \mathbf{U})(\det \mathbf{V}^{\dagger})$
- VI. Compute one-electron and two-electron energy contributions to H_{AB} by making use of CP2K functions for the efficient calculation of the Hartree potential and electron Coulomb energy as well as the *HF* exchange energy. In this step, we make use of the partitioning of the generalized density matrix into a symmetric and an anti-symmetric contribution. The relevant equations in CP2K are highlighted in Appendix B. Finally, compute V_{AB} .

The code is implemented within a fork of publicly available CP2K-6.1 version. An input section "&VAB" provides the *HF* calculation parameters required during the V_{AB} calculation in cases



when the orbitals are not HF orbitals. CP2K's object-oriented design helps in replicating the HF

options under the V_{AB} section. The input section is placed as part of the 'mixed' section as

illustrated below:

```
_____
&FORCE EVAL
&MIXED
. . .
   &VAB
      DO VAB .TRUE.
      &HF
         FRACTION 1.0 !Must be 1.0
         !Other optional sections for setting up HF calculation as in
              !Guidon, et al.'s papers on HF implementation in CP2K 137, 138, 143
          !HF INFO
          !INTERACTION_POTENTIAL
          !LOAD BALANCE
          !MEMORY
          !PERIODIC
          !SCREENING
      &END
   &END
. . .
&END
&END
______
```

In brief, we needed to address two issues. The first one was related to the well-known self-interaction error of DFT that makes it hard to 'localize' electrons. We can use HF and *hybrid DFT* theory that are computationally expensive and at times prohibitive in periodic calculations. Alternately, we can use DFT+U theory that is computationally efficacious and yields charge or spin-localized states. For Hamiltonian operator, we use the exact *n*-electron Hamiltonian (as we would for periodic HF theory) but we used the *n*-electron KS determinants to set the secular equation of eq.(2). In essence, we calculate the HF energy and coupling term of the KS-DFT states. Using the exact *n*-electron Hamiltonian is now computationally affordable owing to the availability of efficient computer codes for periodic calculations that can treat the

28



exact exchange of *HF* theory^{137, 145, 146} and the fact that our *V_{AB}* calculation involves the equivalent of a single *HF* iteration, a very tractable cost. For molecular calculations the formalism is rather straightforward in contrast to periodic calculations that make use of Bloch states with their *k*-points in the first Brillouin zone to account for periodicity.¹⁴⁷ the corresponding orbital transformation may be carried out for each *k* point independently.¹²⁶ The present implementation in the CP2K code¹⁴⁸ deals solely with the Γ point. Source code and inputs for test cases are available at https://github.com/pavankum/cp2k-vab.

As mentioned above, the calculation cost is that of a single iteration of HF calculation. For a bulk system finding the optimized geometry at HF level consumes lot of computation power and practically very difficult. The computation cost of HF is $O(n^4)$, where n is the number of basis functions. So, with our approach we bring down the cost and here are the speedups that can be achieved for every step of HF that is avoided by doing a DFT level calculation of the system:

	Time for one step of HF energy evaluation in cpu hours	Average time for one step of gopt with DFT+U in cpu hours	Speedup based on execution times (HF/DFT+U)	# of sph. ERIs calculated	# of sph. basis fns
Hematite	19388.9	6	3154	1.57E+13	3348
TiO2	15565	2	6396	8.69E+11	1620
BVO	3723	8	466	1.72E+11	1080

Table 2-2 Speedup that can be achieved per step if HF treatment is replaced with DFT level theory for V_{AB} calculation.

Parallel performance of V_{AB} calculation is demonstrated, in figure 2-3 below, with increase in number of processors. The speedup is evaluated with p=4 number of processors as the base case



since the runs with p=1 with this parallel code are slower and that shows a false super-linear speedup. The number of processors is scaled accordingly by dividing with 4 in the graph. This shows very good strong-scaling performance.



Figure 2-3 Speedup showing strong-scaling performance in V_{AB} calculation.

The drop in the computation time with increase in processors is shown in figure 2-4 for the case of linear chain of iron with 7 units described in section 2.3.3.





Figure 2-4 Computation time with respect to increase in processors.

2.3 Application Examples

In this section we describe test calculations that can be compared with calculations performed with other codes or previously published calculations. The systems include He-He⁽⁺⁾, Zn-Zn⁽⁺⁾, a one-dimensional model of iron oxide, hematite Fe₂O₃, and TiO₂ rutile. Lastly we calculate V_{AB} for an electron polaron transfer in BiVO₄, a semiconductor with strong photocatalytic efficiency.^{85, 86} All the pictorial representations of atomic systems were made using VMD visualization software.¹⁴⁹

2.3.1 He₂⁺ dimer

We calculated the electronic coupling for electron transfer in a helium dimer cation He-He⁽⁺⁾ using the *HF* level of theory in CP2K and our new implementation of V_{AB} . We selected a minimal basis set ¹⁵⁰ for these all-electron calculations. Results at different inter-nuclear distances were validated against the Hondo implementation¹⁰¹ and are shown in Table 2-2. The data show excellent numerical agreement with the molecular code (differences less than 10⁻⁴ of the magnitude of V_{AB} , in particular ~ 0.1 cm⁻¹ out of ~5000 cm⁻¹). What matters here is the excellent numerical accord. These results validate the correctness of the new V_{AB} module based on the Coulomb engine in CP2K.





Figure 2-5. He_2^+ electronic coupling calculated in CP2K via the COT method with **HF** orbitals, compared with HONDO values for the same method.

He-He ⁽⁺⁾	СР2К	CP2K	HONDO	HONDO
r (Å)	V _{AB} [cm ⁻¹]	Sab	V _{AB} [cm ⁻¹]	Sab
2.0	5373.714	5.1471E-01	5373.820	5.1472E-01
2.5	1754.505	1.5906E-01	1754.527	1.5907E-01
3.0	550.378	4.9504E-02	550.381	4.9505E-02
3.5	167.995	1.5075E-02	167.995	1.5075E-02
4.0	48.060	4.3110E-03	48.060	4.3105E-03
5.0	2.425	2.1647E-04	2.425	2.1789E-04
6.0	0.051	4.5515E-06	0.051	4.5927E-06

Table 2-3. He_2^+ electronic coupling calculated in CP2K via the COT method with **HF** orbitals, compared with HONDO values for the same method.

$2.3.2 \ Zn_2{}^+ \ dimer$

We calculated the electronic coupling V_{AB} for electron transfer in a zinc dimer cation, Zn-Zn⁽⁺⁾, again using the *HF* level of theory in CP2K. The hole occupies the *4s* atomic states of Zn in the left-localized and right-localized states. Both all-electron and pseudopotential calculations were performed, and results are given in Table 2-3.





Figure 2-6. Electronic coupling V_{AB} and overlap S_{AB} calculated for Zn_2^+ with CP2K via the COT method using **HF** orbitals in this work, compared to **cDFT** orbitals in ref. 109 and the **GMH** formalism in ref. 97.

We used the DZVP-ALL basis set provided with CP2K ¹⁵⁰ for the all-electron calculations. We also used the zinc GTH pseudopotential ¹⁵¹⁻¹⁵³ and associated basis set with 12 valence electrons. The two levels of theory, GAPW and GPW that use pseudo potentials yield results in very close numerical accord. The all-electrons results are somewhat larger. We attribute this fact to the basis set which is different between the all-electron and the pseudopotential calculations. The values of V_{AB} decrease with increasing inter-nuclear distance. Our calculations are in good qualitative accord with the work of Wu and Van Voorhis using cDFT¹⁰⁹ and the work of Cave and Newton using the Generalized-Mulliken-Hush (GMH) approach.⁹⁷

Zn- Zn(⁺)	GAPW All electron	GAPW with Pseudo- potential	GPW with Pseudo- potential	cDFT	GMH
	This work	This work	This work	Ref. 109	Ref. 97
R(Å)	V _{AB} [cm ⁻¹]	V _{AB} [cm ⁻¹]	V _{AB} [cm ⁻¹]	V _{AB} [cm ⁻¹]	V _{AB} [cm ⁻¹]



5.0	1468.753	1227.365	1227.216	1245.491	1593.386
6.0	445.603	279.808	279.797	303.899	474.065
7.0	124.676	56.300	56.300	74.560	136.733
8.0	30.781	8.720	8.720	13.908	37.530
9.0	6.635	1.006	1.006	3.301	9.657
	SAD.	SAD.	S and		
	OAB	SAB	JAB		
5.0	6.1150E-01	6.7675E-01	6.7675E-01		
5.0 6.0	6.1150E-01 1.8670E-01	6.7675E-01 1.5434E-01	6.7675E-01 1.5433E-01		
5.0 6.0 7.0	6.1150E-01 1.8670E-01 5.2945E-02	6.7675E-01 1.5434E-01 3.2611E-02	6.7675E-01 1.5433E-01 3.2611E-02		
5.0 6.0 7.0 8.0	6.1150E-01 1.8670E-01 5.2945E-02 1.3147E-02	6.7675E-01 1.5434E-01 3.2611E-02 5.1359E-03	6.7675E-01 1.5433E-01 3.2611E-02 5.1358E-03		

Table 2-4. Electronic coupling V_{AB} and overlap S_{AB} calculated for Zn_2^+ with CP2K via the COT method using **HF** orbitals in this work, compared to **cDFT** orbitals in ref. 109 and the **GMH** formalism in ref. 97.

2.3.3 One-dimensional periodic iron oxide chains

We used CP2K to calculate V_{AB} in one-dimensional periodic chains of 7, 9, and 11

Fe(OH)₂(H2O)₂⁽⁺⁾ units with one excess electron, following the work of Bylaska and Rosso. ¹²⁶ The excess electron was localized on one of the Fe^{III} atoms making it Fe^{II}, thus the net effective charges on the 7-, 9-, and 11-unit cells were +6, +8, and +10 respectively. In these model systems, the iron atoms are in ferric high spin $3d^5$ states. The localized character of the *A* and *B* states was monitored through the Mulliken spin population of the Fe 3d atomic shells, high spin $3d^4$ for Fe(II) with the localized electron vs. high spin $3d^5$ for Fe(III). The lengths of the respective unit cells were 21.385 Å, 27.495 Å, and 33.605 Å in the X-direction. In the Y- and Z-

directions, we used a box size of 35 Å.



The calculations were done using the *GPW* method and the *HF* level of theory for direct comparison with Bylaska-Rosso.¹²⁶ A truncated potential with cutoff radius equal to half of the smallest cell parameter was used for both *HF* and *V*_{AB} calculations. A modified DZV basis set ¹⁵⁰ (in which we removed the *f* polarization functions from the Fe basis set, the *d* functions from the O basis set, and the *p* functions from the H basis set) and GTH pseudopotentials ¹⁵¹⁻¹⁵³ were used for Fe, O and H atoms. The results are given in Table 2-4.



Figure 2-7. Structure of the ferric oxide 1D-model with 7 units. The system is periodic. The excess electron is localized on the third Fe atom in state A and transfers to the fourth Fe atom in state B (as depicted with the blue arrow). The orange spheres are Fe atoms, the red spheres are O atoms, and the white spheres are H atoms.

In these calculations (and the calculations below for hematite, rutile, and bismuth vanadate), we calculated the nine intermediate points along the selected reaction pathway, in addition to calculating states θ (state A) and I (state B). ΔG^* given in the table refers to the energy of the mid-point along the 'reaction pathway'. λ is the reorganization energy which is the energy gap between the left-localized state at its optimized geometry (state θ) and the right-localized state at the optimized geometry of state θ . In accord with Marcus theory, ΔG^* and $\lambda/4$ ought to be equal when the states are quasi-diabatic, with a harmonic potential, and the ET process is thermoneutral (localized on a single site). That this is the case in our calculation can be seen in Table 2-4. The adiabatic barrier is equal to ($\Delta G^* - V_{AB}$).



1D Fe ^(III) model (<i>HF</i> theory)	7 units (this work)	9 units (this work)	11 units (this work)	7 units (ref. 97)	9 units (ref. 97)	11 units (ref. 97)
$\Delta G^* (eV)$	0.531	0.544	0.528	0.562	0.544	0.607
λ/4 (eV)	0.521	0.539	0.518	0.521	0.528	0.524
V_{AB} (eV)	0.257	0.239	0.265	0.218	0.222	0.226
Adiabatic barrier (eV)	0.273	0.305	0.263	0.326	0.340	0.381
Overlap S _{AB}	0.088	0.081	0.091			

Table 2-5. V_{AB} for ET of an electron polaron in a 1D periodic chain $[Fe(OH)_2(H2O)_2^{(+)}]_n$ with n=7, 9, and 11 units calculated with the **HF** level of theory. ΔG^* is the relative energy of the mid-point along the reaction pathway, λ is the reorganization energy, **V**_{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$)

In Figure 2-8 we display the alternating character of the Fe-(OH) bonds along the chain for the

CP2K optimized electron polaron state localized on a Fe atom at the middle of the 11-unit chain



Figure 2-8 Fe-OH bonds along the chain. The localized excess electron is at position **0**. The distances in the 7- and 9-unit systems are not distinguishable from those of the 11-unit system. obtained with the *HF* level of theory. The results are in good agreement with the work of Rosso and Dupuis¹⁵⁴ and Bylaska and Rosso¹²⁶, all of them using *HF* theory but different basis sets.



The polaronic wave of bond length alternations attenuates at ~ five Fe atoms away from the reduced Fe atom.

For the 7-unit system, we used also the BLYP+U level of theory^{155, 156} with different +U values on the *3d* atomic orbitals of Fe. The results are shown in Table 2-5. Here the wavefunction accounts for some electron correlation effects, leading to a lowering of the diabatic barrier. With increasing +U values (on Fe), the overlap S_{AB} decreases, a sign that the excess electron resides in an orbital that is more and more tightly localized.

	BLYP+U,	BLYP+U,	BLYP+U,	BLYP+U,	BLYP+U,	BLYP+U,
	U = 5	U = 6	U = 7	U = 8	U = 9	U = 10
$\Delta G^* (eV)$	0.443	0.444	0.443	0.441	0.469	0.469
λ/4 (eV)	0.405	0.407	0.383	0.391	0.424	0.425
V_{AB} (eV)	0.127	0.172	0.178	0.178	0.171	0.160
Adiabatic barrier (eV)	0.317	0.273	0.265	0.263	0.297	0.310
Overlap S _{AB}	0.329	0.179	0.115	0.084	0.063	0.048

Table 2-6. **V**_{AB} for a periodic chain of 7-units [Fe(OH)₂(H2O)₂⁽⁺⁾]₇ calculated with BLYP+U orbitals and different +U value. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, **V**_{AB} is the electronic coupling, and the adiabatic barrier is equal to $(\Delta G^* - \mathbf{V}_{AB})$

2.3.4 Bulk hematite Fe₂O₃

We calculated V_{AB} for electron transfer in the basal plane of bulk hematite, using the BLYP+U orbitals level of theory. A 3x3x1 supercell was used with cell parameters [a=14.725 Å, b=14.725 Å, c=13.267 Å], and [α =90, β =90, γ =120]. A modified DZV basis set ¹⁵⁰ (DZVP basis set without *f* polarization functions on Fe and without *d* functions on O) was used for both Fe and O atoms along with GTH pseudopotentials.

An excess electron was localized on one of the Fe atoms as state *A* and on a neighbor Fe atom in the basal plane as state *B*. We used +U_{eff} values = 6.0 eV, 8.0 eV, and 10.0 eV applied to the *3d* orbitals of Fe. Iordanova *et al.* ⁹² reported a value of $V_{AB} \sim 0.19$ eV for a basal plane hop



in high spin configuration, to be compared to ~ 0.04 eV obtained here. We note that the reorganization_energy calculated with BLYP+U increases with the value of +U. It remains smaller than with the *HF* theory. The diabatic barrier ΔG^* is found to be somewhat smaller with periodic BLYP+U theory than with cluster *HF* theory. *V*_{AB} is smaller with BLYP +U compared with cluster *HF*. Overall the accord is satisfactory given the differences in levels of theory between the two calculations (cluster *HF* vs. periodic *BLYP*+*U*), in basis sets, and lastly in the use of a cluster model for the *V*_{AB} calculation by Iordanova *et al.* ⁹²



Figure 2-9. Fe₂O₃ hematite supercell with layers of spin-up [cyan ■] and spin-down [green ■] densities on Fe^{III} atoms. The hop between two Fe atoms in a basal plane is marked in blue color. For clarity, the spin density contours are turned off for the down spin in the top picture. The orange spheres are Fe atoms, the red spheres are O atoms.

Hematite	BLYP+U,	BLYP+U,	BLYP+U,	HF cluster
Fe ₂ O ₃	U = 6 eV	U = 8 eV	U = 10 eV	Ref. 92
$\Delta G^* (eV)$	0.218	0.265	0.290	0.380
λ/4 (eV)	0.200	0.253	0.294	0.355
V_{AB} (eV)	0.040	0.042	0.045	0.190



Adiabatic barrier (eV)	0.178	0.223	0.245	0.190
Overlap S _{AB}	0.023	0.016	0.011	

Table 2-7. V_{AB} for electron transfer in basal plane for bulk hematite from BLYP+U orbitals using CP2K. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, **V**_{AB} is the electronic coupling, and the adiabatic barrier is equal to (ΔG^* - **V**_{AB}).

2.3.5 Bulk rutile TiO₂

This test calculation involved V_{AB} for electron transfer in the *c*-direction for bulk rutile TiO₂. We used a *DFT*+*U* level of theory based on the PBE exchange correlation functional. ¹⁵⁷ We used the SZV basis set ¹⁵⁰ for both Ti and O atoms to generate the localized states in a 3x3x5 supercell



Figure 2-10 Rutile TiO₂ with an iso-surface of the spin density of an electron localized on a Ti atom. The hop between two Ti atoms is marked in blue color in the [001] direction. The silver spheres are Ti atoms, the red spheres are O atoms, green spheres are the polaronic Ti atoms. [a=13.869 Å, b=13.869 Å, c=14.907 Å], [α=90, β=90, γ=90]. The results obtained for different

+U values on the *3d* atomic shell of Ti are shown in Table 2-7.

Rutile TiO ₂	U = 6 eV	U = 8 eV	U = 10 eV	ref. 119
$\Delta G^* (eV)$	0.269	0.275	0.280	0.288
$\lambda/4$ (eV)	0.263	0.274	0.281	0.288



V_{AB} (eV)	0.230	0.149	0.129	0.200
Adiabatic barrier (eV)	0.039	0.126	0.152	0.088
$\frac{ S_{AB} }{ S_{AB} }$	0.061	0.003	0.017	

Table 2-8. V_{AB} for electron transfer in the c-direction for bulk TiO₂ from PBE+U orbitals. ΔG^* is the energy of the mid-point along the reaction pathway, λ is the reorganization energy, V_{AB} is the electronic coupling, and the adiabatic barrier is equal to ($\Delta G^* - V_{AB}$).

Deskins et al. ⁹³ reported V_{AB} values of ~ 0.2 eV for a *c*-direction hop from cluster calculations. Our calculated value is of the same order of magnitude. In particular, there is a good match between the λ reorganization energies.

2.3.6 Bulk ms-BiVO₄

Our last test calculation involves V_{AB} calculation for an electron polaron transfer in bismuth vanadate BiVO₄ (BVO). BVO is a semiconductor that exhibit promising performance toward overall water splitting.⁸⁵ In previous work we characterized electron polaron and hole polaron transport in monoclinic ms-BVO, obtaining the reorganization energy with plane wave periodic PBE+U wavefunctions and V_{AB} with a small model cluster *HF* calculation.⁸⁵ Here our calculation was for an electron polaron transfer from a V atom to a nearest neighbor in the (021) direction in bulk BVO.

We used a DFT+U level of theory based on the PBE exchange correlation functional. ¹⁵⁸ We used the SZV basis set¹⁵⁰ for both V and O atoms to generate the localized states in a 3x3x1 supercell [a=15.587 Å, b=15.281 Å, c=11.704 Å], [α =90, β =90, γ =90.383]. The results obtained for different +U values on the *3d* atomic states of V are shown in Table 2-8. The calculated





Figure 2-11 ms-BiVO4 with an iso-surface of spin density for an electron localized at a V atom. The hop between two V atoms is indicated in blue color. The green spheres are polaronic V atoms, silver spheres are V atoms, the red spheres are O atoms, and purple spheres are Bi atoms.

values of V_{AB} and of the diabatic activation barrier are in good accord with our earlier work. In

particular, V_{AB} is small.

	DDEILI	DDEII
BiVO	PDE+U	PDE+U
DI V 0 4	U = 6 eV	U = 8 eV
$\Delta G^* (eV)$	0.295	0.305
λ/4 (eV)	0.295	0.288
V_{AB} (eV)	0.010	0.040
Adiabatic	0.285	0.265
barrier (eV)	0.265	0.203
Overlap S _{AB}	0.113	0.078

Table 2-9. V_{AB} for electron transfer in the (021) direction in bulk BiVO₄ from PBE+U orbitals. ΔG^* is the energy of the mid-point along the hopping pathway, λ is the reorganization energy, **V** to is the electronic coupling, and the adiabatic herrier is equal to (ΔG^* , **V** to)

 V_{AB} is the electronic coupling, and the adiabatic barrier is equal to (ΔG^* - V_{AB}).

2.4 Conclusion

In this chapter we reported a new implementation of a method for the calculation of the

electronic coupling matrix element VAB of ET theory in periodic systems. We presented test

calculations that highlight the capability of the new module that is embedded in the CP2K code,

as described in the section 2. The capability allows the complete characterization of ET in the

solid state via the two localized quasi-diabatic state Marcus/Holstein model of polaron. It can be

المنسارة للاستشارات

41

used for any single determinant representation of the electronic structure of the system from HF, DFT, hybrid DFT, DFT+U, or cDFT theory. Results are given for several test systems including iron oxide models, hematite Fe2O3, titanium dioxide TiO2, and bismuth vanadate BiVO4. The computer code re-uses several of the high-performance computing functions of CP2K. The method requires only the equivalent of one iteration of an HF calculation. The ability to calculate HAB for localized states allows the complete treatment of polaron transport in semiconductors at the periodic *DFT* level of theory.



Chapter 3 Maximal Orbital Analysis: Superexchange interactions in solid state

3.1 Introduction

Here, we are concerned with a periodic DFT formulation of the Maximal Orbital Analysis (MOA) to characterize super-exchange interactions in ET the solid state. Given a wavefunction, the MOA method defines the maximal projection of the wavefunction onto a subgroup of atoms. Of special interest is to analyze the tail of localized state wavefunctions onto linker bridge fragments. The wavefunction tail defines the extent of electronic coupling in ET. We highlight results for ET in mixed-valent metal complexes, and e - / h + polarons hopping in the solid state.

Electron transfer (ET) in transition metal compounds due to photoexcitation, or in biological compounds in a solution, is greatly influenced by surrounding ligands. ET can be through-space or via the bridging anions. ^{38, 159} For transfer pathways involving non-magnetic anions (since all the anion shells are filled) superexchange model holds. Orbitals involved in superexchange are helpful in determining the extent and strength of the interaction between the polaronic states during ET.^{91, 92, 160} Interpreting those electronic interactions and energy transitions, from the wavefunctions, is made possible by various population analysis methods.¹⁶¹

The (MOA) theory ¹⁶² is a variant of population analysis methods, wherein the best possible projection of the variational molecular orbitals on a fragment atomic basis is done. In the context of ET, such a projection helps in assigning how much of the tail of a localized wavefunction of initial state (donor) overlaps with that of a final state (acceptor), which is another way of



approximating coupling without explicit calculation. Thus, MOA is advantageous to check how different anions affect superexchange, or, when multiple ET pathways are possible, to quantify which pathway is more favorable based on the bridging atom fragments, or, lastly, how much increase in electron transport can be expected based on dopants and percentage of doping. In general, MOA occupations provide a useful picture of electron sharing between donor and acceptor.

A more detailed background on population analysis methods, comparisons with MOA, and various applications are presented in the initial formulation by Dupuis, et al.¹⁶² Here, a more generic implementation of the method that extends its capability to periodic calculations is done in CP2K, a quantum chemistry and solid state physics software package that can perform atomistic simulations.^{133-137, 140, 150, 151, 153, 163-165} Results for selected molecular and solid-state periodic systems are presented.

3.2 MOA Formulation and Implementation

The key part of MOA formulation is a corresponding orbitals transformation ¹⁴ defined between orthonormal molecular orbitals $|\varphi\rangle$ from any level of (Hartree-Fock or DFT) spin-polarized theory, and a subset of basis functions $|\chi^B\rangle$ of any chosen fragment. This transformation is unitary in nature and does not alter the wavefunction or its energy. When multiconfigurational methods are used care must be taken not to mix active space and inactive space orbitals which would result in wavefunction and energy changes. Maximal overlap is guaranteed by the inherent property of the corresponding orbitals transformation. The overlap matrix is:

$$P = \langle \chi^B | \varphi \rangle$$



44

The unitary transformations $|\tilde{\chi}^{B}\rangle = |\chi^{B}\rangle V$, and $|\tilde{\varphi}\rangle = |\varphi\rangle U$ diagonalize the matrix P, at the same time as maximizing the diagonal elements. U and V are matrices of eigen vectors of the matrices PP[†], and P[†]P respectively.

$$\tilde{p} = U^{\dagger}PV$$

Here, the U matrix rotates the fragment basis set functions and the V matrix rotates the molecular orbitals. We can build a wavefunction from these transformed atomic or fragment MOA orbitals. The diagonal elements of \tilde{p} are essentially occupation numbers of these new 'corresponding' orbitals. Implementation-wise we start with an atom-centered spherical harmonic basis (ASH) and a set of transformations are performed to build the projection matrix P, with a 'molecule-orthonormalized – fragment-orthonormalized - atom-centered orthonormalized spherical harmonics basis (MOFOAOSH) and the molecule-orthonormalized molecular orbitals:

$$P = \langle \chi^{MOFOAOSH} | \varphi^{MO} \rangle$$

We refer the reader to the appendix of Dupuis, et al.,¹⁶² for more details into the transformations involved. This wavefunction analysis is implemented in CP2K,^{133, 163} a periodic plane-wave code widely used in solid-state community. Input section is placed under the property calculation section, and information on each tag is provided in the appendix. Reiterating that the only inputs that are needed for this subroutine are molecular orbitals and overlap matrix, the back-transformed MOA orbitals in the atomic spherical harmonic basis are used to build the wavefunction and evaluated over a "Gaussian cube" for use with an external visualization software.

In some cases, by doing COT on alpha and beta orbitals we can isolate excess orbitals. The TiO_2 example below demonstrates it in detail.



3.3 Results and Discussion

3.3.1 Water-dimer

🖌 للاستشار

MOA implementation in CP2K is validated with Hondo^{144, 166, 167} implementation for simple molecules and a good agreement is found. One such testcase is the water dimer molecule shown in Figure 3-1. Out of the two water molecules, one is a donor of the hydrogen bond (the water molecule on the left), and the other is an acceptor (the water molecule on the right).



Figure 3-1. Water dimer with the hydrogen bond depicted by a dotted red line between the donor on the left and the acceptor on the right.

MOA results reproduced with the new implementation in CP2K for a closed shell HF optimized geometry and 6-31G** basis set, ¹⁶⁸ are presented here. Each water molecule comprises 24 Spherical Gaussian basis functions. The water dimer system has 10 molecular orbitals: two orbitals for the 1s electrons of each oxygen atom; two orbitals for the 2s electrons of each of the oxygen atom; two orbitals for a 2p lone pair of electrons on each of the oxygen atom; and two pairs of two OH(σ) orbitals for the OH bonds of each of the water molecules. If a fragment of only the left water molecule is chosen for MOA projection, then we end up with 10 non-zero eigen values after diagonalizing the matrix PP⁺ giving us the best representation of the water dimer electron density captured by the "donor" water basis set only.

Donor	λ	$occ = 2\lambda^2$		Acceptor	λ	$occ = 2\lambda^2$
		_	16			
	4		40			

1	1.0000	2.0000	1	1.0000	2.0000
2	1.0000	2.0000	2	1.0000	1.9999
3	1.0000	1.9999	3	1.0000	1.9998
4	0.9999	1.9997	4	0.9996	1.9982
5	0.9971	1.9882	5	0.9814	1.9263
6	0.2551	0.1301	6	0.0738	0.0109
7	0.0300	0.0018	7	0.0124	0.0003
8	0.0096	0.0002	8	0.0072	0.0001
9	0.0057	0.0001	9	0.0052	0.0001
10	0.0004	0.0000	10	0.0003	0.0000

Table 3-1. MOA occupations in water dimer at HF(6-31G**) optimized geometry



Figure 3-2. MOA orbitals #5 and #6, in spherical harmonic basis, for the donor water molecule. Orbital #5 on the left is a OH (σ) orbital, and #6 is a OH (σ *) orbital that has a node between the oxygen and hydrogen involved in h-bonding.

Similarly, when the second water molecule is chosen as a fragment, then we are projecting onto the "acceptor" basis set only. Table1 shows the occupation numbers for the donor and acceptor fragments, the first five on each side show higher occupations as expected, which are the orbitals of the respective water molecules. The five at the bottom are the overlaps of the acceptor orbitals on the donor basis functions and vice versa. Figure 3-2 shows the MOA orbitals 5 and 6, in spherical harmonic basis, for the left side water monomer. Donor orbital #5 is a OH (σ) orbital,



47

and donor orbital #6 is a OH (σ^*) orbital that has a node between the oxygen and hydrogen involved in hydrogen bond. The results of Dupuis, et al.¹⁶² for water dimer are well reproduced here and further details are avoided for the sake of brevity.

Periodic solids

To analyze the ET behavior qualitatively in periodic solid-state systems and show the possible uses of MOA we chose titania TiO2, hematite Fe_2O_3 , and a 1D- $Fe^{(III)}$ chain of ferric ions as test cases.

3.3.2 TiO2 system

MOA is done for atom fragments of an electron-localized Ti atom, its neighbor Ti, and the two bridging O atoms in bulk rutile TiO₂, which are highlighted in Figure 3. We used a DFT+U level of theory based on the PBE exchange correlation functional. ¹⁵⁷

Atom	SZV	DZV	DZVP
Ti	[s, s, p, d] = 10 bfns	[s, s, s, p, p, d, d] = 19 bfns	[s, s, s, p, p, d, d, f] = 26 bfns
0	[s, p] = 4 bfns	[s, s, p, p] = 8 bfns	[s, s, p, p, d] = 13 bfns

Table 3-2. Number of basis functions in different basis for Ti and O.

We used SZV basis set ¹⁵⁰ for both Ti and O atoms to generate the localized states in a 3x3x5 supercell [a=13.869 Å, b=13.869 Å, c=14.907 Å], [α =90, β =90, γ =90]. A +*U* value of 10 eV is added to the titanium 3d orbitals and Mulliken method of +U is used for geometry optimization. GTH pseudopotentials ¹⁵¹ are used for both titanium and oxygen wherein for titanium there are 12 valence electrons corresponding to [$3s^2 3p^6 3d^2 4s^2$], while for oxygen there are 6 valence electrons representing the outer shell [$2s^2 2p^4$]. Taking these optimized geometries single point



energy calculations are done to do MOA, by switching to Lowdin method of +U, with SZV, DZV and DZVP basis to gain insights on orbitals involved in superexchange. Table 2 gives the number of basis functions present in each of the basis sets used here.



Figure 3-3. Bulk rutile TiO2. We are interested in looking at the electron sharing when it is localized on one of the Ti atoms highlighted here.

	Neutral			Charged		
Fragment	POP	CHRG	SPIN	POP	CHRG	SPIN
Ti - target for electron						
localization	10.805	1.195	0.000	10.871	1.129	1.023
Ti neighbor	10.804	1.196	0.000	10.818	1.182	0.008
bridging O-O atoms	13.191	-1.191	0.000	13.194	-1.194	-0.015

Table 3-3. Population, charge, and spin from MOA for the specified atom fragments when all the molecular orbitals are projected on their respective basis functions within SZV.

Table 3 show a comparison between the neutral and electron localized states' MOA for the projection of all the molecular orbitals onto different atom fragments within the minimal basis SZV. There are 10 basis functions for Ti in SZV and hence in neutral configuration Ti⁺⁴ is



expected to have higher occupations in the four orbitals that correspond to $3s^2 3p^6$ atomic orbitals of Ti, which can be seen in Table 4. In charged state when an excess electron is added we have Ti⁺³ and we can see higher occupation in alpha orbital #5. From the orbital picture we can confirm that the excess electron goes into a 3d orbital.

Atom fragment: Ti which is a target for electron localization	Neutral		Charged state		
MOA Orb. #	alpha	beta	alpha	beta	
1	0.999	0.999	0.999	0.999	
2	0.999	0.999	0.999	0.999	
3	0.999	0.999	0.999	0.999	
4	0.996	0.996	0.997	0.996	
5	0.366	0.366	0.991	0.246	
6	0.334	0.334	0.269	0.235	
7	0.255	0.255	0.254	0.228	
8	0.169	0.169	0.242	0.088	
9	0.168	0.168	0.102	0.083	
10	0.119	0.119	0.096	0.051	
Total	5.402	5.402	5.947	4.924	

Table 3-4. MOA occupations when all orbitals are projected on the Ti atom which is a target for electron localization. An excess electron in alpha channel is marked in red for the charge localized state.

Table 5 shows the MOA occupation when all the orbitals are projected onto the bridging oxygens' basis functions. There is a total of 8 basis functions in SZV, 4 each for the two oxygens forming the bridge between the two Ti atoms as shown in Figure 3. Since all the orbitals are filled we can't notice discernable differences between the occupation numbers in Table 5.

Atom fragment: bridging OO atoms	Neutral	Charged state
	50	

MOA Orb. #	alpha	beta	alpha	Beta
1	0.895	0.895	0.894	0.896
2	0.865	0.865	0.855	0.858
3	0.858	0.858	0.852	0.853
4	0.838	0.838	0.839	0.843
5	0.820	0.820	0.819	0.824
6	0.777	0.777	0.812	0.811
7	0.773	0.773	0.770	0.770
8	0.770	0.770	0.749	0.749
Total	6.595	6.595	6.589	6.605

Table 3-5. MOA occupations when all orbitals are projected on the bridging O atoms involved in ET. Since all the orbitals are filled no significant difference can be observed here between neutral and charged states.

This necessitates isolating the excess electron orbital so that we can clearly see electron sharing with the bridging oxygens. Again, COT comes to the rescue. We can separate the excess orbital by constructing natural orbitals with COT on the alphas and betas thereby allowing for a maximal pairing. All the paired-up electrons result in a non-zero overlap whereas the unique unpaired orbital will have a diagonal element of zero. Now if we do MOA with this single orbital we will get an exact picture of electron sharing between the electron-localized Ti, the transfermediating oxygens and the neighbor Ti atoms. We will find only a single value of moa occupation because of a single orbital projection on the atom fragment basis that corresponds to excess charge. Table 6 shows the single moa-occupation values within different bases.

Atom Engement	SZV	DZV	DZVP
Atom Fragment	SPIN	SPIN	SPIN
Ti - target for electron localization	0.938	0.953	0.929
Ti neighbor	0.004	0.003	0.004
bridging O-O atoms	0.016	0.011	0.020



Table 3-6. MOA with only the excess electron orbital projected onto the different fragments in SZV, DZV, and DZVP bases.

Figure 4 shows the wavefunction plots of excess electron orbital projected onto the basis functions of electron-localized Ti atom. There is no difference in the orbital picture when additional diffuse functions are added to the basis. All of them show a d-orbital occupation as expected and there are no surprises here.



Figure 3-4. MOA orbital of the excess electron when projected onto the electron-localized Ti basis functions within SZV, DZV, DZVP.

When the same excess orbital is projected onto the bridging oxygen basis functions we see interesting results. These are the orbitals that are involved in superexchange. For SZV and DZV there are no d-functions and superexchange happens via p-orbitals. Although the top and bottom oxygen are anti-symmetric here we can see that in the DZV case the diffuse functions are in-





Figure 3-5 MOA orbital of the excess electron when projected onto the electron-localized Ti basis functions within SZV, DZV, DZVP. Note that all orbitals are defined within a +/- sign (phase). A phase difference can be seen for SZV and DZV. For DZVP, the contributing atomic function is now a d function, in contrast to the p function for SZV and DZV.

phase with the compact p-orbitals and there are no nodes. When it comes to DZVP the dfunctions on oxygen facilitate superexchange as evident from the wavefunction plot in Figure 5. If we look at the eigen vector components for this excess orbital projection on the oxygen atoms' basis the p-orbitals are antisymmetric with each other for the two oxygens. The sign difference between O1 and O2 in Table 7 represents that. In the case of DZV and DZVP p_x , p_y and p_z have the same sign for both the compact and diffuse orbitals indicating that there are no nodes.


Eigen	vec. for e	xcess orbit	al projectio	on onto t	he OO-br	idge basis	functions
O #1	SZV	DZV	DZVP	O #2	SZV	DZV	DZVP
S	0.127	-0.123	0.039	S	0.127	-0.123	0.039
рy	0.036	-0.567	-0.269	рy	-0.036	0.567	0.269
pz	0.110	-0.492	-0.118	pz	0.110	-0.492	-0.117
px	0.036	-0.567	-0.269	px	-0.036	0.567	0.269
S	—	0.244	0.027	S	—	0.244	0.027
рy	_	-0.431	0.269	рy	_	0.431	-0.269
pz	-	-0.885	0.443	pz	_	-0.885	0.443
px	_	-0.431	0.269	p _x	_	0.431	-0.269
d -2	-	_	0.230	d -2	-	—	0.230
d -1	—	_	-0.093	d -1	_	_	0.093
\mathbf{d}_{0}	_	_	-0.418	\mathbf{d}_{0}	_	_	-0.418
d +1	—	_	-0.093	d +1	_	_	0.093
d +2	—	—	0.000	d +2	—	—	0.000

Table 3-7. Eigen vector components corresponding to the excess orbital projection onto the basis of two bridging oxygens.

Another interesting aspect to check is whether along a Marcus curve electron sharing increases or not with the neighbor atoms involved in transfer. For this purpose, MOA is done with DZVP basis and the unique excess orbital is projected onto the different fragment basis functions at two geometries, state0 as well as the crossing point.



	U=10 eV	U = 6 eV	U = 4 eV
State 0 geometry	SPIN	SPIN	SPIN
Ti - target for electron localization	0.929	0.897	0.850
Ti neighbor	0.004	0.009	0.018
bridging O-O atoms	0.020	0.025	0.027
Crossing point geometry	SPIN	SPIN	SPIN
Ti - target for electron localization	0.920	0.872	0.735
Ti neighbor	0.006	0.018	0.081
bridging O-O atoms	0.025	0.030	0.034

Table 3-8. MOA occupations along a Marcus curve for qualitative analysis. Increase in electron sharing is observed between the state0 and crossing point geometries. It is more evident with lower +U value.

It is to be noted that these geometries correspond to a different activation barrier and this analysis with different +U and a different basis set is solely for qualitative insights. With a higher +U of 10 eV there is no significant change in the moa occupations at state0 and crossing-point geometries. It can be attributed to the diabatic nature from higher +U value. Lowering +U values to 6 eV and 4 eV we can see increased sharing of the excess electron with O-O bridge and neighbor Ti atom.

3.3.3 Hematite Fe₂O₃

MOA to analyze ET behavior in the basal plane of bulk hematite, using the BLYP+U orbitals level of theory is done. ¹⁵⁶ A 3x3x1 supercell was used with cell parameters [a=14.725 Å, b=14.725 Å, c=13.267 Å], and [α =90, β =90, γ =120]. DZV basis set was used for both Fe and O atoms along with GTH pseudopotentials ¹⁵¹ for the optimized geometries. Iron has 19 basis functions from [s, s, s, p, p, d, d], whereas oxygen has 8 basis functions from [s, s, p, p]. Pseudopotential on Fe has 16 valence electrons corresponding to [3s² 3p⁶ 3d⁶ 4s²], while on oxygen 6 valence electrons representing [2s² 2p⁴] Hematite is made up of spin-up and spin-down



Fe(III) atoms layer by layer. It is not possible to isolate the excess electron orbital here using COT as we did in TiO_2 case above. Yet, we can look at moa occupations since the orbitals right after the filled ones are key to superexchange.

Encomont		Neutral		Charged			
Fragment	POP	CHRG	SPIN	POP	CHRG	SPIN	
Fe - target for electron localization	16.119	-0.119	-4.243	16.285	-0.285	-3.676	
Fe neighbor	16.120	-0.120	-4.242	16.125	-0.125	-4.235	
bridging O-O atoms	11.818	0.182	-0.001	11.788	0.212	0.169	

Table 3-9. MOA occupations comparison between neutral and electron-localized states for Hematite.

Table 9 shows a summary of population, charge and spins due to projection of all the molecular orbitals onto the basis functions of the specified atom fragments. Comparison with neutral state values is shown. Table 10 gives the moa occupations for the electron-localized Fe atom both in charged state and when there was no charge in neutral configuration.

For spin-down Fe(III) valence shell configuration is [3s² 3p⁶ 3d⁵], and hence in neutral system we can see from Table 10 that there are 4 alpha and 9 beta orbitals with higher occupation numbers. The excess electron is localized in one of these layers and it goes into an alpha state. From the wavefunction plots we can see that the moa orb #4 in charged state corresponds to the excess electron occupied alpha d-orbital. Orbital plot is shown in Figure 6.

Atom	Neutral	Charged
fragment: Fe target for	(Fe III)	(Fe II)



electron								
MOA Orb.		alpha		beta		alpha		beta
1	3р	0.982	3p	0.992	 3p	0.983	3p	0.988
2	3p	0.980	3p	0.992	3p	0.980	3p	0.988
3	3p	0.980	3p	0.992	3p	0.980	3p	0.985
4	3s	0.939	3d	0.990	3d	0.976	3d	0.982
5		0.333	3d	0.990	3s	0.943	3d	0.982
6		0.333	3d	0.983		0.240	3d	0.981
7		0.194	3d	0.980		0.240	3d	0.980
8		0.185	3d	0.980		0.158	3d	0.980
9		0.185	3s	0.941		0.142	3s	0.946
10		0.162		0.203		0.142		0.180
11		0.150		0.203		0.135		0.180
12		0.150		0.181		0.101		0.162
13		0.131		0.160		0.101		0.138
14		0.074		0.154		0.068		0.133
15		0.074		0.154		0.036		0.133
16		0.039		0.083		0.036		0.071
17		0.019		0.082		0.031		0.071
18		0.015		0.082		0.006		0.068
19		0.015		0.040		0.006		0.033
Total		5.938		10.181		6.3045		9.9806

Table 3-10. MOA occupations for all orbitals projection onto electron localized iron atom both before and after excess electron is introduced. Alpha orb #4 marked in red indicates the excess electron whose orbital is shown in figure 6.





Figure 3-6. Wavefunction plots of the moa orbitals in charged state: (1) Excess electron alphaorbital #4 on the electron-localized Fe atom. (2) Beta orbital #9 on bridging oxygen atoms that facilitates superexchange. It shows a node on both oxygens implying the diffuse p-orbitals are out-of-phase between the compact p-orbitals.

It is a bit tricky to get the excess electron contribution on the bridging oxygens since it is not possible to isolate the excess orbital as mentioned before. Two bridging oxygens have 4 fully filled orbitals each, corresponding to $[2s^2 2p^6]$. Hence, we see higher occupation numbers for a combined 8 orbitals in neutral and charged systems. Unfilled orbitals which come after these filled ones and which show significant difference from neutral system can be assumed to be involved in superexchange. Beta orbital #9 shows significant difference with the neutral system orbital among the unfilled orbitals with higher occupation number, and it can be assumed to facilitate superexchange. Wavefunction plot of this orbital shown in Figure 6 depicts p-type orbitals involved. A node is observed here which might relate to the diffuse functions being out of phase with the compact functions.



Atom fragment: bridging OO atoms	Ne	utral	Char	ged	
MOA Orb.	alpha	beta	alpha	beta	
1	0.797	0.796	0.809	0.777	
2	0.776	0.784	0.799	0.763	
3	0.758	0.761	0.767	0.746	
4	0.730	0.727	0.736	0.713	
5	0.709	0.716	0.721	0.702	
6	0.692	0.680	0.696	0.669	
7	0.596	0.582	0.589	0.579	
8	0.568	0.580	0.575	0.574	
9	0.050	0.049	0.052	0.051	
10	0.046	0.046	0.049	0.046	
11	0.043	0.043	0.046	0.044	
12	0.043	0.040	0.040	0.040	
13	0.034	0.033	0.036	0.034	
14	0.028	0.032	0.027	0.030	
15	0.019	0.023	0.021	0.023	
16	0.018	0.019	0.018	0.018	
Total	5.909	5.910	5.979	5.809	

Table 3-11. MOA occupations for all orbitals projection onto the basis function of bridging oxygen atoms. Unfilled beta orbital #9 marked in red shows significant difference with the neutral system and is assumed to facilitate superexchange for ET.

3.3.4 1D-Fe^(III) Chain – 7 units

Hartree Fock (HF) with one-dimensional periodic chain of 7 units of $Fe(OH)_2(H2O)_2^{(+)}$, a model similar to the work of Bylaska and Rosso, ¹²⁶ is another test case of interest. In this model system, the iron atoms are in ferric high spin $3d^5$ states. The excess electron was localized on one of the Fe^{III} atoms making it Fe^{II}, thus the net effective charges on the 7-unit cell being +6. HF



with *truncated*-potential cutoff equal to half the shortest cell dimension is used. DZV basis set is used, like Hematite case above. Here also it is not trivial to isolate the excess electron orbital.

Errogmont		Neutral		Charged		
Fragment	POP	CHRG	SPIN	POP	CHRG	SPIN
Fe - target for electron localization	15.802	0.198	4.750	15.998	0.002	3.904
Fe neighbor	15.802	0.198	4.750	15.854	0.146	4.731
bridging O-O atoms	12.473	-0.473	0.189	12.526	-0.526	0.168

Table 3-12. MOA occupations comparison between neutral and electron-localized states for 1d-
Fe chain.

Summary of moa occupations for projection of all the orbitals onto the basis functions of iron atoms involved in ET and the bridging oxygens is shown in Table 12. For spin-up Fe(III) valence shell configuration is $[3s^2 3p^6 3d^5]$ with 13 electrons. These filled orbitals can be seen in the highlighted 13 high occupation values from Table 13. Additionally, in the charged state excess electron goes into beta channel, as seen in the orb #4 (marked in red). Wavefunction for this excess orbital is shown in Figure 7.

Atom fragment: Fe target for electron localization	Neutral				Charged				
	(Fe III)			(Fe II)					
1	3p	0.996	3p	0.988		3р	0.995	3р	0.991
2	3р	0.995	3p	0.985		3р	0.995	3p	0.988
3	3р	0.994	3p	0.981		3р	0.992	3p	0.984
4	3d	0.992	3s	0.951		3d	0.991	3d	0.983

60

المنسارات

5	3d	0.991	0.298	3d	0.989	3s	0.963
6	3d	0.989	0.258	3d	0.989		0.216
7	3d	0.986	0.190	3d	0.989		0.199
8	3d	0.983	0.177	3d	0.985		0.158
9	3s	0.953	0.171	3s	0.964		0.130
10		0.228	0.147		0.184		0.122
11		0.219	0.116		0.183		0.102
12		0.189	0.092		0.157		0.075
13		0.180	0.087		0.133		0.053
14		0.176	0.036		0.124		0.051
15		0.150	0.030		0.106		0.014
16		0.088	0.015		0.063		0.012
17		0.078	0.002		0.055		0.005
18		0.067	0.001		0.045		0.001
19		0.025	0.001		0.013		0.000

Table 3-13 MOA occupations for all orbitals projection onto electron localized iron atom both before and after excess electron is introduced. Beta orb #4 marked in red indicates the excess electron whose orbital is shown in figure 7.

Evaluating the effect of excess charge on bridging oxygens is difficult in this case too. Projection

of all orbitals onto basis functions of oxygen in both neutral and charged state is given in Table

14. Assuming the highest occupation unfilled orbital is involved in superexchange beta orb #9 in

charged state is a probable orbital for superexchange. But, it is not as evident as in the Hematite

case, the differences are small with other unfilled orbitals.





Figure 3-7. MOA orbitals for all orbitals projection onto Fe and bridging oxygen bases.(1) For the excess electron in orb #4 of beta orbs in Fe. (2) Highest occupation number unoccupied orbital having a bigger difference with neutral state.



Atom fragment: bridging OO atoms	Neut	ral	Charge	d state
	alpha	beta	alpha	beta
1	0.950	0.929	0.947	0.922
2	0.899	0.872	0.905	0.879
3	0.855	0.826	0.878	0.850
4	0.840	0.798	0.852	0.830
5	0.801	0.770	0.776	0.738
6	0.633	0.629	0.655	0.649
7	0.626	0.617	0.616	0.614
8	0.597	0.596	0.598	0.597
9	0.039	0.038	0.042	0.043
10	0.033	0.031	0.025	0.023
11	0.023	0.014	0.023	0.016
12	0.017	0.013	0.015	0.009
13	0.010	0.007	0.008	0.006
14	0.004	0.001	0.004	0.001
15	0.002	0.001	0.002	0.001
16	0.001	0.001	0.001	0.001
Total	6.331	6.142	6.347	6.179

Table 3-14. MOA occupations for all orbitals projection onto the oxygen bridge basis functions. Beta orb #9 marked in red is the highest occupation unfilled orbital and is assumed to involve in superexchange, it is shown in figure 7.

3.3.5 Bismuth Vanadate (BiVO₄)

For ET in Bismuth Vanadate (BVO) along (021) direction, between two Vanadium atoms, the transfer is through-space. In here we used a DFT+U level of theory, with a U_{eff} of 6 eV, based on the PBE exchange correlation functional. ¹⁵⁸ We used the SZV basis set¹⁵⁰ for Bi, V and O atoms to generate the localized states in a 3x3x1 supercell [a=15.587 Å, b=15.281 Å, c=11.704 Å], [α =90, β =90, γ =90.383]. MOA is done for the atomic fragments of Vanadiums involved in



transfer and the surrounding oxygen quartets, shown in Table 15. We can see a significant change in the charge of oxygen quartet around the electron localized Vanadium atom.

Fragment	Neutral			Charged		
Tuginent	POP	CHRG	SPIN	POP	CHRG	SPIN
V1: target for electron						
localization	12.101	0.899	0.000	12.093	0.907	0.999
V2: neighbor	12.101	0.899	0.000	12.100	0.900	0.012
Oxygen quartet around V1	26.097	-2.097	0.000	26.305	-2.305	-0.030
Oxygen quartet around V2	26.097	-2.097	0.000	26.098	-2.098	-0.008

Table 3-15. MOA occupations for the projection of all orbitals onto basis functions of Vanadium and Oxygen fragments involved in ET.

Vanadium is in V^{+5} oxidation state while in neutral configuration, which corresponds to a valence of $[3s^2 3p^6 3d^0 4s^0]$. In minimal basis SZV, we have 10 basis functions, 2 for s, 3 for p and 5 for d. Hence, we see four higher occupation numbers for neutral configuration in the Table 16 that correspond to $[3s^2 3p^6]$. Additionally, when excess electron is introduced we see an additional higher occupation in alpha channel of Vanadium as expected.

Fragment V: electron localized	Neutral		Charged	
MOA Orbs	alpha	beta	alpha	beta



1	0.999	0.999	0.999	0.999
2	0.999	0.999	0.999	0.999
3	0.999	0.999	0.999	0.999
4	0.997	0.997	0.997	0.997
5	0.388	0.388	0.990	0.288
6	0.367	0.367	0.348	0.288
7	0.357	0.357	0.331	0.268
8	0.354	0.354	0.329	0.247
9	0.353	0.353	0.302	0.244
10	0.236	0.236	0.252	0.217
Total	6.051	6.051	6.546	5.547

Table 3-16. MOA occupations for the projection of all orbitals on the basis functions of Vanadium atom targeted for electron localization before and after introduction of excess electron.

Here the excess electron orbital can be isolated by doing COT between the alphas and betas before doing MOA. Table 17 shows the moa occupations for different atomic fragments when only a single orbital with excess electron is projected onto their basis functions.

Fragment	State 0: e [−] is on V1	Crossing point: e ⁻ on V1	State 1: e ⁻ on V2
	SPIN	SPIN	SPIN
V1	0.760	0.736	0.003
V2	0.003	0.004	0.758
Oxygen quartet around V1	0.180	0.187	0.002
Oxygen quartet around V2	0.002	0.003	0.182

Table 3-17. MOA occupations for projection of excess electron orbital onto the basis functions of listed atomic fragments.

From figure 8 we can see how the excess electron is distributed among Vanadium and the surrounding oxygen quartet. The oxygen orbitals here are not mediating ET and it occurs through-space between the Vanadium atoms. Hence the coupling is lower between the two



polaronic states. Not much difference can be observed between the excess charge distributions at state0 and crossing point geometries when electron is localized on V1.



Figure 3-8. Plot of wavefunction when only the excess electron orbital is projected onto the basis functions of Vanadium and its surrounding oxygen quartet.

3.4 Conclusion

MOA is implemented for periodic solid-state calculations. Test cases were presented for bulk rutile TiO2, bulk Fe2O3 and a model system of 1D chain of iron (ferric) units. Excess electron orbital is successfully identified in the case of TiO₂ which gives a perfect underlying picture of charge distribution during ET with well-chosen atomic fragments. Many such systems can benefit from a quick analysis with MAO that captures overlap. It can be a very good metric to assess efficacy of ET among an array of test compounds.



Appendix

Input section of MOA implementation in CP2K (source code is accessible at

https://github.com/dupuislab/CP2K) :

&PROPERTIES

&MOA

NFRG 2	! No. of fragments
LFRG 1 2	! Length of fragments
IFRG 1 2 3	! Atoms in fragments by indices
NOMOA 16 0 0	! Exclude MOs if index is non-zero, default = all are included
NOMOAA 13 0 58	! Can be in mixed format
NOMOAB 17	! If $n_{beta} = 8$, 8^{th} element will be added as zero
IFUNO	! default = .FALSE.
VEC_TOL	! Printing Eig. Vec. Values GE to this, $default = 0.01$
JACOBI_P	! To use Jacobi diag. to construct P matrix ($P=S*V$), default = .FALSE.
&MO_CUBES	! Built wfn from MOA orbs in Sph. Harm. basis
STRIDE 2 2 2	! The stride (X,Y,Z) used to write the cube file
MO_LIST 1 2 3	! List of MOs to print as cube
&END	
&END MOA	
&END PROPERTIES	



Chapter 4 Biased-dynamics for Electron Transfer

4.1 Introduction

Ab initio molecular dynamics (AIMD), or Born-Oppenheimer molecular dynamics, combines electronic structure theory with molecular dynamics (Newton's equations of motion) and is a powerful tool in studying the evolution of a physical system under varying conditions. The forces that propagate a molecular dynamics trajectory are obtained from an electronic structure calculation at every step. Thus, this method is computationally very demanding to calculate the properties of periodic solid-state systems. A typical timestep of AIMD is in the femtosecond range and the polaron hopping events we aim to characterize occur in the nanosecond or longer timescale. This disparity in timescales mean the system spends more time in sampling uninteresting regions of potential energy surface and less time in the more relevant configuration space. In other words, system must escape from 3N-dimensional basins for better sampling of important regions of potential energy. Such infrequent-events can be accelerated by providing an energy boost so that barrier crossing happens more often or by weighted sampling techniques. To name a few methods, umbrella sampling, ¹⁶⁹ hyperdynamics, ¹⁷⁰ metadynamics, ¹⁷¹⁻¹⁷⁵ parallel replica dynamics, ¹⁷⁶ temperature accelerated dynamics, ¹⁷⁷⁻¹⁷⁹ bond boost method of dynamics, ¹⁸⁰⁻¹⁸² are various approaches that have proven useful in observing physical phenomena at larger timescale.

Earlier studies of charge transfer with molecular dynamics by Warshel and coworkers¹⁸³⁻ ¹⁸⁵ used empirical valence bond method to construct effective hamiltonians and the free energy surface is calculated by umbrella sampling. They called the approach an adiabatic charging model wherein running the trajectories on different mapping potentials would gradually force the system to change from the initial state to the final state. In a similar vein, Kerisit and Rosso ¹⁸⁶



68

performed classical molecular dynamics with charging potentials and the vertical energy gap as a reaction coordinate. Blumberger and Sprik ^{187, 188} also used the vertical energy gap as a reaction coordinate along with a constrained ab initio molecular dynamics method. In another work by Blumberger and Sprik, ¹⁸⁹ reactant state and product state equilibrium simulations are done separately and linearly combined to get free energy curves. Recently, Zhou, et al., ¹⁹⁰ performed AIMD for an hematite system Fe₂O₃ and extracted the activation barriers in a similar fashion by interpolating the initial and final state coordinates along the transfer pathway.

In all the works mentioned above, either the vertical energy gap or a linear combination of initial and final state simulations is used to derive the Marcus parameters. Building upon this, we want to make use of the associated bond changes in a solid-state electron transfer reaction to propagate the trajectory. The presence of the excess electron increases the repulsion between the reduced metal ion and the anion atoms. The excess electron goes into an anti-bonding orbital between the M-O (metal-anion bond), which reduces the electron density in the shared region and induces a bond lengthening. It is empirically found that an electron (polaron) transfer results in an interchange of bond lengthening between the initial atomic site and the final site. Taking this into consideration, we defined the bond length changes as collective coordinates and used metadynamics along with a mixed-force umbrella sampling formalism to sample both initial and final states simultaneously, and a combination of forces is used to move the trajectory forward. We chose bulk TiO₂ as our test system.

4.2 Biased dynamics for polaron hopping

Metadynamics ^{171, 191-193} is a biased sampling approach wherein sampling is reduced from 3Ndimensional space to a selective set of collective variables (CVs) that are highly relevant and representative of the physical phenomena we want to observe. Typically, collective variables can



69

be distance-based, or energy function-based, or coordination number-based, or dihedral anglebased, or any such property which is easily quantifiable from the 3N ionic coordinates. The definition of CV should clearly identify the reactant and product states. Sampling is enhanced by slowly adding a time-dependent gaussian bias to the potential energy function, which is a function of the defined CVs, centered along the trajectory leading out of the energy basins. The added bias is accumulated in an external potential term and at time t it is given by:

$$V_{G}(s(x),t) = w \sum_{\substack{t' = \tau_{G}, 2\tau_{G}, \dots \\ t' < t}} exp\left(-\frac{\left(s(x) - s(x_{G}(t'))\right)^{2}}{2\delta s^{2}}\right)$$
(4.1)

where *w* is the height of the gaussian, δs is the width of the gaussian, τ_G is the deposition rate of the gaussians or the time interval at which a new gaussian is added, and *x* represents the trajectory coordinate. Here, $x_G(t')$ represents the trajectory under the action of $V+V_G$, *V* being the normal free energy surface. As $\tau_G \rightarrow 0$, and for *d* number of CVs, rewriting the above summation in integral form we have

$$V_G(s(x),t) = \int_0^t dt' \,\omega \, exp\left(-\sum_{i=1}^d \frac{\left(s_i(x) - s_i(x_G(t'))\right)^2}{2\delta s_i^2}\right)$$
(4.2)

where, ω is the energy rate which is gaussian height divided by deposition rate (w/τ_G). So, the total potential energy of the system in terms of the coordinate space $x = (r, \tilde{s})$, where *r* are the actual coordinates and \tilde{s} are the auxiliary variables is,

$$V(x) = V(r) + \frac{1}{2}k(\tilde{s} - s(r))^2 + V_G(\tilde{s}, t)$$
(4.3)

The free energy surface (FES) within the collective variable space as $t \to \infty$ is therefore given by,



$$F(s) = -\frac{1}{\beta} \ln\left(\int dx \exp(-\beta V(x)) \delta(s - s(x))\right)$$
(4.4)

The error in FES reconstruction is assessed to be ¹⁷¹

$$\varepsilon \propto \sqrt{\frac{\omega}{D\beta}}$$
 (4.5)

where, D is the intrinsic system diffusion coefficient in CVs space.

The advantages of meta-dynamics are:

- the sampling of rare events is accelerated by adding a boost, and it discourages revisiting configurations that are already sampled
- it allows exploring new reaction pathways since the approach does not place a constraint on the reaction coordinate. The system can escape the energy basins passing through the lowest free-energy saddle point
- no a priori knowledge of the potential energy surface is required
- underlying free energy surface is the inverse of biasing potential

There are few drawbacks too with the meta-dynamics method:

- it requires fine-tuning the gaussian width, height and deposition rates which severely impact the sampling rate
- finding the definition of 'good' CV is not easy
- when to stop the meta-dynamics run is not trivial; the general rule of thumb is as soon as initial and final state energy basins are filled, the system starts sampling a flat surface and it is ideal to stop then. As more bias is added, the system may start sampling higher energy regions which makes it difficult to interpret the FES.



71

As mentioned before, electron transfer events are characterized by significant elongation and compression of bonds around the electron localized metal site and its neighbor respectively. For example, the figure below highlights a cluster of titanium atoms (extracted from the periodic solid) and their surrounding oxygens that are involved in a c-direction electron transfer pathway in bulk rutile TiO₂. It shows the increments and decrements from a neutral system in its ground state configuration when an excess electron is placed on a titanium atom.



Figure 4-1. Bond increments and decrements in angstroms around titanium atoms in bulk rutile TiO₂ when an excess electron is localized on the left and right metal atoms in state 0 and state 1 respectively.

We can observe a flip in the bond increments and decrements when the excess electron transfers from the left to the right titanium atom in the above figure. A set of four variables V1, V2, V3, and V4 are defined as average changes in bond increments for a corresponding pair of Ti-O bonds as shown in the figure below.





Figure 4-2. Collective variable definition

To incorporate the flipping of bond changes with the occurrence of an electron transfer, the four variable set defined before is reduced to a set of two collective variables with which metadynamics is carried out. These two collective variables are the differences CV1 = (V1 - V4) and CV2 = (V2 - V3) since the increments and decrements are observed in these pairs (V1, V4) and (V2, V3) among the previously defined averages. When the ground state equilibrium structures are observed the range of collective variable values for state 0 and state 1 are as follows:

	State0	State1
$\mathbf{CV1} = (\mathbf{V1} - \mathbf{V4})$	0.06	-0.06
CV2 = (V2 - V3)	0.15	-0.15

Table 4-1. Collective variable values in initial and final states

These values show a clear distinction between the initial and final states which is the first and foremost quality of a 'good' collective variable definition.

Now we are set to do meta-dynamics in this reduced variable space. For a smooth transition near the saddle point we included an umbrella sampling energy function which is a linear combination of both the initial and final electron localized states. It is possible to do this mixed-force dynamics calculation in CP2K.



At each point on the trajectory electronic structure calculations for both states are performed, let us call the states A and B, and the combined umbrella sampling ¹⁹⁴ energy function to propagate the dynamics is defined as:

$$E_U = -k_B T \ln \left(e^{-\beta E_A} + e^{-\beta E_B} \right) \tag{4.6}$$

The forces that drive the molecular dynamics with this energy function are

$$F_{U} = F_{A} \frac{e^{-\beta E_{A}}}{e^{-\beta E_{A}} + e^{-\beta E_{B}}} + F_{B} \frac{e^{-\beta E_{B}}}{e^{-\beta E_{A}} + e^{-\beta E_{B}}}$$
(4.7)

Here, E_A and E_B are the biased energies from meta-dynamics, whereas E_U is the umbrella sampling energy that combine both states.

Smoothening of the energy surface at the transition point is shown in Figure 4-3 below, with the E_U surface plotted in green. At the crossing point the energy is $k_BT*ln(2)$ lower than the original diabatic crossing point, a difference that is usually very small when compared to the actual barrier. The purpose here is to avoid the discontinuity in forces when a transition to other state happens.





Figure 4-3 Graph showing how umbrella sampling energy function from equation 4.6 would allow a smoother transition at the crossing point

A constraint in the form of quadratic walls is placed on the other sides of the energy minima along the reaction coordinate so that the system samples the region of interest, which includes mainly the transition.

In Figure 4-4 a schematic of the overall system is depicted where we have the filling of an energy basin with the metadynamics gaussian hills, umbrella sampling function smoothening the transition near the crossing, and the quadratic walls placed on either sides of the energy minima to confine the sampling to the region of interest. In essence, we are sampling along the green line and the free energy surface (or potential of mean force) is obtained by removing the gaussian bias added, as given in equation 4.4.



75



-E_A -E_B -E_U -left wall -right wall

Figure 4-4 Schematic of the metadynamics along with an umbrella sampling function (in green) for smooth transition near the crossing point region, and quadratic walls on both sides to constrain the dynamics to region of interest.

4.3 Hyperparameters and computational details

The gaussian bias defined in equation 4.2 is a function of the width (δs) and height (w) of gaussian, gaussian deposition rate (τ_G), and the timestep of the molecular dynamics run. Time step (Δt) of an ab initio molecular dynamics run is dependent on the inherent timescales of the electronic and nuclear motions. For a nice discussion on the choice of time step we refer the reader to Marx and Hutter. ¹⁹⁵ The timescale of nuclear motion can be ascertained from the highest phonon or vibrational frequency τ_n , which is usually of the order of 10⁻¹⁴ seconds or 10 femtoseconds (for a maximum frequency of 4000 cm⁻¹). To get a good accuracy while integrating the equations of motion an upper limit on the timestep would be ideally $\Delta t^{max} \approx \tau_n/10$. We chose a timestep of 0.5 femtoseconds in our simulations to avoid instabilities in force computation that arise due to a poor choice of time step during the numerical integration of Newton's equation of motion.



For the gaussian height, we tested $1/10^{\text{th}}$, $1/20^{\text{th}}$, and $1/40^{\text{th}}$ of the original diabatic activation barrier of 0.28eV in bulk TiO₂ for a c-dir hop in ground state. The knowledge of an estimate of the barrier is not needed in general, but we were testing how the choices affect the metadynamics run. Similarly, we considered the gaussian widths of 0.1, 0.05 and 0.02, keeping in view of the collective variable values from Table 4-1. Deposition rates of every 20, 50 and 100 timesteps were used in different runs. Figure 4-5 below shows one of these runs with bad parameters.

We used a SZV basis set ¹⁵⁰ for both Ti and O atoms, and a 3x3x5 supercell with the cell parameters [a=13.869 Å, b=13.869 Å, c=14.907 Å], [α =90, β =90, γ =90]. A +U value of 10 eV is added to the titanium 3d orbitals. GTH pseudopotentials ¹⁵¹ were used for both titanium and oxygen wherein for titanium there are 12 valence electrons corresponding to [3s² 3p⁶ 3d² 4s²], while for oxygen there are 6 valence electrons representing the outer shell [2s² 2p⁴]. System is initially equilibrated to 300 K in NVT ensemble for 2.5 picoseconds. A velocity rescaling thermostat (CSVR) with a small time constant of 1 is used to induce strong thermostating.



Figure 4-5 Energy convergence in an equilibration run of 2.5 picoseconds.



Figure 4-5 shows that the system is well equilibrated as the changes in energy are minimal and of the order of 10^{-5} atomic units. This well equilibrated trajectory is used for doing production runs with the biased potential applied.

4.4 Results and Discussion

The figure below shows the free energy surface reconstructed from a metadynamics trajectory of 16.4 picoseconds. A single hop is observed, and symmetric energy basins can be seen from the contour plot with centers that fall near the expected ground state minima.

One major issue with this run is the position of crossing point, which is deep at \sim -0.4 eV. In an ideal case the crossing point would be slightly below zero when we have a good sampling near the transition region. Since there is only one hop observed the system went through the saddle point only once and we need more such crossings to get a well-defined surface there. Frequent crossings happen across the transition plane once the free energy surface flattens due to the added bias.



Another reason for this discrepancy is due to the wider gaussians that add a bias in transition region while the trajectory is still in one of the basins and thus bring the barrier down. One way to avoid this is to place narrower gaussians that would actually fill the transition region only *when the trajectory is at the transition region*. A small caveat is that when a gaussian width is narrowed down then we must compensate for the slow sampling either by increasing the height



Figure 4-6 a, b.) Free energy surface of a 16.4 picoseconds trajectory with a poor choice of the parameters gaussian width $\delta s=0.1$, height $w=0.007 \ eV$, deposition rate $\tau_G=100$. Two symmetric basins are formed as seen in the contour with a barrier of 0.05 eV. c.) A flip in the bond lengths observed during a hop at around 8.7 ps.

of gaussian or by faster deposition. The distance between the transition state and localized state minima, barrier-wise and in terms of collective variables, need to be considered regarding the size of gaussians, for their height and for their width.



One more major issue here is the stopping criteria for adding gaussians. If we continue adding the bias even after filling the basins we end up with the situation in figure 4-6. An adaptive bias must be applied, or we should turn off the bias manually after inspecting the evolution of the free energy surface.

In the figure 4-8, we show a better choice of metadynamics parameters that reduces this effect of dragging down of crossing point. Here, we observe two hops through the transition region, and the energy basins are better resolved than the previous one above.





Figure 4-7 a,b.) Free energy surface of a 11 picoseconds trajectory with the parameters gaussian width $\delta s=0.05$, height $w=0.014 \ eV$, deposition rate $\tau_G=100$. Two basins are formed, where one seems to have a minimum near the ground state minimum and the other is approaching towards

it. A barrier of 0.13 eV is observed, there is still a bit of dragging down near the transition region. c.) Two hops are observed during the run at around 1 and 7.7 ps. d.) corresponding bond length changes reflecting the hops are shown here.



4.5 Conclusion

Metadynamics with the bond length based collective coordinates can represent the polaron hopping characteristics very well. It shows promise in accelerating the hop events and estimating the activation barrier. The only drawback is the 'tuning' of the hyper-dynamics parameters which can severely affect the free energy surface generation, and oftentimes deter the objective. However, we believe that the parameters 'tuned' for TiO2 may be a good starting point for other metal oxides semiconductors as they all exhibit similar phonon frequencies and vibrational densities of states. Shallow gaussians with faster deposition rates are much preferred and an adaptive self-learning bias needs to be applied.



Chapter 5 Compressed Sensing for phonon modes of charge transfer

5.1 Introduction

Phonons are quantized elastic waves that arise from the lattice vibrations. The presence of an excess charge alters certain vibrational modes due to polaron formation in many of the transition metal compounds. As we have seen in previous chapters, charge transfer is associated



Figure 5-1. Marcus diagram for two different systems with different electron transfer modes resulting in changed activation barriers

with significant distortions in lattice structure, which appear as an anti-phase symmetric breathing mode dynamics. ^{18, 93} A concerted decrease in bond lengths around the initial polaron site and increase in bond lengths around the final site, makes it one of the key descriptors that represent the physical phenomena of charge transfer and helps in estimating activation barriers.^{191, 192, 196} From Fig. 5-1 and comparing the softer 'red' and stiffer 'blue' surfaces, we can see that the stiffness of the potential energy surfaces modulates the activation energy for hopping. The important parameters that enter the evaluation of the activation barriers, the reorganization energy λ and the coupling element V_{AB}, are computationally very expensive. We aim to explore the possibility of isolating the charge transfer breathing phonon mode from the



vibrational phonon spectrum to estimate more easily the activation barrier. Methods to obtain this phonon mode are described in the section below, and they help in the direct computation of mobility.

Ab initio molecular dynamics (AIMD) removes the potentially significant approximation of the two-state model i.e., the use of an ad-hoc reaction pathway and the restriction of harmonicity (harmonic potential energy surfaces). The anti-phase symmetric breathing mode corresponds to the underlying reaction pathway in the two state polaron hopping model.^{18, 50} Molecular dynamics captures this correlated atomic motion which can be transformed as vibrational spectrum.¹⁹⁷ The Fourier transformation of the Velocity Auto Correlation (VAC) function calculated from AIMD is a well-established methodology to get the power spectrum. A potentially much more efficacious approach is to use Compressed Sensing^{15, 198} of the velocity auto correlation function to get the vibrational frequency spectra with much shorter MD trajectories.

5.2 Compressed sensing

Compressed sensing (CS) allows reconstruction of a signal from reduced a number of samples. Here the sparsity occurs in the limited number of sampling points of the molecular dynamics. With a shorter trajectory we can only access the higher frequencies and it is a question of how to determine the full spectrum, including the slow modes, when we have only a few thousands of 'configurations' (sets of 3N coordinates). In the most basic approach we use a quadratic approximation and calculate 6N gradients that gives us the force constant matrix (dynamical matrix). In contrast, MD gives the frequencies in the non-quadratic approximation although sampling all modes is quite expensive.



84

When applied to transforming the real-time data of molecular dynamics simulations to frequency domain we hope to extract information about the electronic and nuclear dynamics in a much more efficient way than with the use of standard discrete Fourier transform. Reduction in computation time by a factor of five is reported by Andrade, et al.¹⁵

Traditional method is to project time-resolved velocity autocorrelation function v(t) on to vibrational frequency domain $g(\omega)$ by cosine transform

$$g(\omega) = \int_{-\infty}^{\infty} dt \cos(\omega t) v(t)$$

In discrete formulation,

$$g_k = \sum_{j=1}^{N_t} \Delta t \cos(\omega_k t_j) v(t_j)$$

The resolution of all frequencies requires lengthy simulations to sample configuration space properly.

We reformulate the above problem as:

$$Fg = v$$

where, \mathbf{F} = Fourier matrix of size N_t X N_w. For short simulation times N_t < N_w, the linear system is underdetermined, and we have many possible solutions for **g**. *Since many of the Fourier coefficients are zero the problem reduces to finding the sparsest solution which is equivalent to a basis pursuit denoising problem* of minimizing the *l*1 norm of the objective function **g**

$$\min_{\boldsymbol{g}} |\boldsymbol{g}|_1$$
 subject to $|\boldsymbol{F}\boldsymbol{g} - \boldsymbol{v}| < \eta$

where η is the noise level. The Spectral Projected Gradient method for *l*1 minimization (SPGL1) is a code developed by Friedlander *et al.*,¹⁹⁸ to carry out the minimization. We employed this compressed sensing methodology to obtain the vibrational (phonon) spectrum of our systems (in lieu of Fourier transform). Spectral projected gradient methods differ from Quasi-Newton



methods in the selection of step length that results in efficient convergence for large scale optimization problems. The choice of step lengths is related to the spectrum of the underlying local Hessian rather than related to the standard decrease in the objective function value.¹⁹⁹

5.3 CS for resolution of ET phonon modes

The vibrational spectrum obtained from molecular dynamics of an excess electron localized rutile TiO2 system using CP2K is shown in figures 2 and 3. A supercell of 3x3x5 and SZV basis sets for Ti and O are used. A CSVR thermostat is used to maintain the temperature at 300 K. For the same system harmonic normal modes from small displacement method at T=0 K using the computer code 'phonopy' with CP2K are obtained (and shown in Figure 5-3). A small shift in frequencies can be observed due to anharmonicity via temperature in molecular dynamics.







www.manaraa.com



Figure 5-2. Time evolution of vibrational spectrum of electron-localized TiO2 obtained from Compressed sensing (left column, blue) compared with Fourier transform (right column, green) of the velocity autocorrelation function from an MD trajectory within NVT ensemble at 300K temperature.

From Figure 5-2 it can observed that 3ps of trajectory gives a well-converged spectrum in case of compressed sensing whereas FFT did not resolve many of the frequencies yet. There does not



appear to be a large difference between the spectra at 3 ps and 4 ps in the case of compressed sensing that shows a good convergence within a shorter trajectory of 3 ps. Figure 5-3 shows the error convergence compared to the longer 4 ps trajectory. Here CS does not appear to be significantly more powerful than FFT.





www.manaraa.com


Figure 5-3 Error in intensities at different times with respect to 4ps spectrum respectively for CS and FFT. Here $\delta I = I(t) - I(t=4 \text{ ps})$ on the y-axis.

A comparison of vibrational spectra obtained by compressed sensing on a molecular dynamics trajectory (at T=300K), and via the finite displacement method (at T=0K) for differences of



gradients using 'phonopy' (phonopy is quadratic approximation compared to MD that gives a non-quadratic approximation of the energy surface) with CP2K is shown in figure 5-4.



Figure 5-4. Vibrational spectrum of electron-localized TiO2 obtained from the Compressed sensing of velocity autocorrelation function of MD trajectory within NVT ensemble at 300K temperature. Phonon spectrum in red is obtained by small displacement method at T=0 K using phonopy. ¹ Shifts in frequencies with MD trajectory are observed when compared to phonopy output because of anharmonicity due to temperature.

Figure 5-5 shows the phonon spectra of a subset of atoms that form two TiO6 octahedrons, one with an electron localized on a Ti atom and the six oxygen atoms surrounding it, and the second 'neutral or stoichiometric octahedron that is a far-way Ti atom with its surrounding oxygen atoms, which represents the bulk of the solid (each octahedral subset consists of 7 atoms in total here). We can see a small shift of frequencies near 500, 600 and 800 cm⁻¹ for the electron-localized Ti octahedron when compared to the distant bulk-representative octahedron. The whole range of vibrations seems to be shifting for the charge localized octahedron, but it remains difficult to pick up a set of dominant frequencies. A similar effect is



noticed if we calculate the vibrational spectrum of the Ti-O stretches, instead of individual atom movements, in these octahedrons, shown in Figure 5-6.



Figure 5-5 Phonon spectra of <u>subset of atoms</u> that form two octahedrons, first of which is an electron-localized Ti atom and the six oxygen atoms surrounding it, second octahedron is a faraway Ti atom and surrounding six oxygen atoms that represent the bulk.

Figure 5-8 shows the combined phonon spectra of two octahedrons that are involved in electron transfer, which is a subset of 12 atoms (as shown in Figure 5-7). Among the 12 atoms two are Ti atoms, which are neighbors involved in c-dir electron hop. And a total of 10 surrounding oxygen atoms for the two Ti atoms, with 2 oxygens forming a bridge. Two frequencies near 450 and 500 cm⁻¹ stand out in Figure 5-8.





Figure 5-6 Phonon spectra of <u>Ti-O stretches</u> that form two octahedrons; first of which is an electron-localized Ti atom and the six Ti-O bonds surrounding it; second octahedron is a faraway Ti atom and surrounding six Ti-O bonds that represent the bulk.



Figure 5-7 Octahedrons of Ti and surrounding oxygen atoms in a TiO2 lattice. Ti atoms are in grey color and Oxygens are in red.





Figure 5-9 Phonon spectra of two octahedrons combined which makes it a <u>subset of 12 atoms</u>; two of which are Ti atoms involved in electron transfer, one Ti has an electron localized and the other is its neighbor; and the surrounding 10 oxygens, two of which are bridging the Ti atoms.



Figure 5-8. Phonon spectra of <u>**Ti-O bond stretches**</u> in two octahedrons combined, which makes it a total of 12 bonds; six Ti-O bonds around the Ti that has an excess electron localized and the others are around the neighbor Ti atom.

Figure 5-9 shows a similar trend in spectrum with two frequencies standing out, for the Ti-O bond stretches, instead of the individual atom movements, although shifted by 100 cm⁻¹.



5.4 Conclusion

Even though slightly better resolution of peaks is observed with compressing sensing when compared to the method of Fourier transform, the CS approach is not significantly better than the FFT approach, as had been remarked in the case of isolated molecules presented in Andrade et al. ¹⁵ There are a large number of vibrations in the range of 0 to ~ 1000 cm⁻¹ (density of states) in a crystal lattice that deters this method to be as effective as small molecules wherein the number of vibrations are much smaller and better separated. Sparsity plays a very important role in the effectiveness of compressed sensing methodology and it seems even for a small subset of atoms in a periodic crystal there are too many coupled vibrational modes, rendering the method not as powerful in the solid state, contrary to anticipations.



Chapter 6 Materials Screening Based on Electron Transport

6.1 Introduction

High throughput materials screening approaches for solar energy materials are severely inhibited by the large number of rules that need to be applied for modeling each of these compounds. There are several underlying processes that contribute in different ways to the overall material functionality. A typical high throughput workflow thus involves tiered screening wherein we start out with a set of layered descriptors that describe the macroscopic property or functionality. Thus, a target property has multiple descriptors, and initial filters consist of easily computable descriptors so that we can train a model, and then use the model to predict the property for a large set of materials. For example, while estimating conductivity of energy conversion materials, their band gap must fall within the visible range of solar radiation, and applying this filter brings down the number of compounds from millions of possibilities to thousands. A classic example involves the class of 'perovskites' which are earth-abundant transition metal compounds that have excellent potential to be photoconversion materials. The total number of possible combinations with different space groups and different stoichiometries is huge. If we constrain the search to one specific space group and a single stoichiometry, such as ABX₃, then we end up with more than 36,000 possible combinations. Korbel, et al., ²⁰⁰ filtered over 32000 of such perovskites with cubic crystallographic structure based on thermodynamic stability, band gap, and hole effective masses to nearly 200 compounds with better conductivity. Some of these 200 compounds include novel materials combinations that have not been synthesized previously, resulting in the discovery of potential candidates with good performance.

One caveat here is the method used for quantifying transport. in their work, the authors used the average effective mass of excited electrons. The authors clearly mentioned that this



approximation of single-band model for the effective mass did not account well for mobility due to the existence of degenerate bands. Also, it is known that the effective mass model does not really apply to small polarons that are carriers in most oxides. It is a challenging choice to decide how much detail should be incorporated while performing thousands of calculations with minimal human intervention and within accessible computation power. Electron transport is difficult to model, and a part of our effort was focused on deriving descriptors that correlate effectively with transport and design principles to screen transition metal compounds.

6.2 BMX₃ dataset

We started with a systematic study of chalcogenide perovskites, having stoichiometric formula BMX₃, in distorted structure that are easy to synthesize via liquid processing. ²⁰¹ Here B, M and X are given by:

- B barium,
- M titanium, zirconium, hafnium (Group IV)
- X oxygen, sulfur, selenium (Group VI).



Figure 6-1 BMX₃ compounds in distorted perovskite structure, where B=Ba, M=Ti/Zr/Hf, and X=O/S/Se.





Figure 6-2 Bandgaps of BMX₃ set of compounds.

Electron and hole transfer barriers were calculated for the metal and anion respectively within Marcus theory linear approximation using VASP ²⁰²⁻²⁰⁶ at PBE+U level of theory. ¹⁵⁸ A 2x2x1 supercell is used and a gamma centered k-point grid of dimensions 2x2x2 is used, along with a plane-wave cutoff of 400 eV. Dudarev's method of +U is chosen to treat the strong on-site coulomb interaction. ¹²³ A +U value of 6 eV is applied to the metal atoms for electron transfer calculations, and a +U value of 10 eV is applied to the chalcogens for hole transfer calculations. The structures are optimized up to force convergence of 0.01 eV/A and energy convergence of 1.0E-05 eV. Gaussian smearing method with a width of 0.05 eV is used for smooth convergence. PAW-PBE pseudopotentials are used and the valence configurations are as follows: ²⁰⁷

 $Ba_sv-10\ electrons-5s^2\ 5p^6\ 6s^2$

 $Ti_sv - 12 \; electrons - 3s^2 \; 3p^6 \; 4s^2 \; 3d^4$



 $Zr_{sv} - 12 \text{ electrons} - 4s^2 4p^6 5s^2 4d^4$ Hf_sv - 12 electrons - 5s^2 5p^6 6s^2 5d^4 O - 6 electrons - 2s^2 2p^4 S - 6 electrons - 3s^2 3p^4 Se - 6 electrons - 4s^2 4p^4

In BMX₃, there are three identical pathways for both electron and hole transfers, as illustrated in Figire 6-1, with the barriers shown in the following bar graphs. Missing data are due to the difficulty in obtaining localized configurations in those compounds for that transfer.



Figure 6-3 Electron polaron transfer barriers in BMX₃ set of compounds.





Figure 6-4 Hole polaron transfer barriers in BMX₃ set of compounds.

Some preliminary observations from this small dataset are as follows:

- sulfur and selenium containing compounds show higher electron and hole mobility than oxygen containing compounds
- \checkmark lower energy barrier and higher mobility with Hf over Zr

These simple observations emphasize that the chemical environment of an electron or hole polaron carrier, and how effectively they are 'bound' to the lattice atoms determine the mobilities. A more thorough analysis can be made by including descriptors that broadly fall into the following categories:²⁰⁸

- 1. Chemical composition
- 2. Band structure
- 3. Elemental properties
- 4. Structural properties

Before going into a detailed list of relevant descriptors for electron transport in perovskites we need to generate a large dataset of transfer barriers. From Korbel, et al., ²⁰⁰ we have a filtered set



of nearly 200 cubic perovskite compounds that have potential for higher mobility. Taking the chemical formula of this screened set of compounds as a starting point to study electron transport patterns, a job builder script has been written. The following tasks are in mind when creating a workflow for screening the materials:

- 1. Get the compound's optimized structure from aflowlib ^{5, 209, 210} using its API
- 2. With the same set of calculation parameters (cutoff, +U value, pseudopotential, etc.), localize an excess electron by elongating the bonds around a specific metal site
- 3. Check whether a localized state is obtained or not after the DFT calculation.

These tasks proved difficult to automate as localized states are not obtained with ease. Differing magnetic properties of compounds resulting in weird spins, and delocalization of electron even with application of a higher +U value are detrimental to achieve any automation of this task. Charge localization still requires lot of attention and parameter tuning for each compound. It was not possible to create a generalized set of parameters that could be applied in this context. Another attempt was made by fixing the distorted GdFeO₃ structure as the base structure for all materials in the selected compound space and then optimized the neutral structures in the first step. In a second step, a higher +U value was used to get a good localized initial guess for the localization jobs. Even with these tricks, the excess charge got delocalized in most of the cases.

As it was proven to be a challenging if not tedious task to make a set of rules for charge localization and get the transfer barriers in a linear approximation, we opted for an alternative approach to identify descriptors. We collected already available small polaron transport data from the literature and from our calculations of BMX₃ to create a dataset of 26 compounds for electron polaron transfer shown in Table 6-1 below.





Figure 6-5 Training set of electron transfer barriers collected from literature as well as calculated by us.

	Compound	Activation Reference	
		barrier in eV	
1	ZrO2	0.20	Christine ²¹¹
2	ZrOS	0.14	Christine ²¹¹
3	BiVO ₄	0.37	Liu, et al. ²¹²
4	CeO ₂	0.40	Plata, et al. ²¹³
5	α-Fe ₂ O ₃	0.19	Iordanova, et al. ⁹²
6	Ta ₃ N ₅	0.21	Morbec, et al. ²¹⁴
7	α -Cr ₂ O ₃	0.21	Iordanova, et al. ⁹¹
8	TiO ₂	0.09	Deskins, et al. 93
9	FeO	0.17	Kerisit, et al. ¹⁸⁶
10	Fe ₃ O ₄	0.19	Skomurski, et al. ⁷⁴
11	NiO	0.32	Yu, etal. ⁷⁶
12	LiFePO ₄	0.22	Maxisch, et al. ²¹⁵
13	MnPO ₄	0.20	Maxisch, et al. ²¹⁵
14	FePO ₄	0.18	Maxisch, et al. ²¹⁵
15	FeBO ₃	0.14	Loftager, et al. ²¹⁶
16	α-MoO ₃	0.17	Ding, et al. ²¹⁷



17	BHSe	0.05	This work
18	BZSe	0.10	This work
19	BZS	0.04	This work
20	BTSe	0.11	This work
21	BTS	0.13	This work
22	ВТО	0.29	This work
23	HfO ₂	0.06	Munoz, et al. ²¹⁸
24	LiMnO ₂	0.30	Hoang ²¹⁹
25	Li ₂ MnO ₃	0.33	Hoang ²¹⁹
26	MnO	0.47	Hoang ²¹⁹

Table 6-1. Electron polaron activation barriers collected from literature

6.3 Chemical Descriptors for ET

While considering what factors weigh into the conductivity of a solar energy conversion material we can start with a fundamental question of what makes a material to be metallic or insulating in the first place. We need chemical descriptors that quantify electron affinity and its movement in a bulk lattice. Here is a set of potential descriptors that affect polaron formation and its mobility in a transition metal compound:²²⁰

- 1. Bond energies of diatomic cation-anion D_298/(kJ/mol)^-1
- 2. Oxidation state of cation
- 3. Coordination number of cation
- 4. Ionic radius of cation
- 5. Ionic radius of anion
- 6. Effective Electronegativity (Using Sanderson's principle of electronegativity equalization)
- 7. Electronegativity of metal in ion form



- 8. Electronegativity of anion in ion form
- 9. Covalent radius of cation
- 10. Covalent radius of anion
- 11. (Oxidation state)th IP of cation [Example: 4th IP of Ti implies IP of Ti+3]
- 12. Second or third electron affinity of anion
- 13. Electron affinity of anion
- 14. Metal anion stretching frequency
- 15. Bader net charge on cation
- 16. Bader net charge on anion
- 17. U`o (electron excitation energy as defined in Torrance, et al. ²²⁰)
- 18. Distance between metal-anion (d_MO)
- 19. Molecular weight
- 20. Number of d valence filled in cation
- 21. Number of f valence filled in cation
- 22. Reduced mass of cation-anion pair
- 23. Bond elongation due to excess electron around metal atom (Δx)

Most of the structural data is accessed from the aflowlib ⁵ and materials project ⁸ repositories while the elemental properties are from NIST data accessed through the python packages QCElemental, and Magpie. ¹⁰

6.3.1 Multicollinearity among descriptors and feature selection

In multivariate regression, one descriptor variable can sometimes be highly correlated with others i.e., it can be linearly predicted from the others with a substantial degree of accuracy. This regression pitfall is called multicollinearity. The precision of the estimated regression



coefficients decreases as more predictors are added to the model. So, we need to eliminate these redundant descriptors by few heuristics such as:

1). **Detection from linear models:** Large changes in regression coefficients when data is added or deleted is an indicator. Insignificant regression coefficients in multiple regression correspond to the affected variables.

2). <u>Variance inflation factor (VIF)</u>: It is the ratio of overall regression model variance with multiple descriptors, divided by the variance of the model with each individual descriptor term. Typically, a VIF less than five is good and greater than 10 indicates severe multicollinearity among the descriptors.

3). <u>Condition number</u>: This test indicates the potential sensitivity of the computed inverse to small changes in the original matrix. Condition number > 15 is a concern, >30 is a serious concern. ²²¹

4). **Pearson correlation:** Construction of a correlation matrix among the descriptor variables will yield indications as to the likelihood that any given pair of right-hand-side variables are creating multicollinearity problems (this describes a bivariate relationship, whereas collinearity is a multivariate phenomenon). An absolute value in the range 0.7 to 1.0 implies strong linear correlation, 0.5 to 0.7 implies a moderate linear correlation, 0.3 to 0.5 means a weak linear correlation and 0.3 to 0.0 means little or no association between the variables. Applying these principles to the list of descriptors mentioned above and removing the highly

correlated descriptors along with recursive feature elimination, and finally using random forests estimator, we arrived at the top 10 relevant features for ET as shown in the table below.

	Descriptor	VIF
1.	Electron excitation energy (U`o in eV)	2.68
2.	EN of metal in ion form	3.36
3.	M-O stretching frequency	3.80



4.	EN_Sanderson	3.86
5.	Molecular weight	4.04
6.	d_MO	5.08
7.	bond energies of diatomic cation-anion	5.48
8.	(Oxdn. state) [^] th IP of cation	6.85
9.	Reduced mass of cation-anion pair	7.54
10.	Bader net charge on cation	8.47

Table 6-2 Top 10 descriptors and sorted according to their variance inflation factors. The condition number of the matrix with the top 10 descriptors is 9.71, which is good.

6.4 Model comparison and Results

For the supervised learning algorithm, we have a wide variety of choices and here we tried linear regression, polynomial ridge regression, random forests and gradient boosting. Gradient boosted decision trees model performs better as we can see from Table 6-3, with low mean squared error among all.





Figure 6-6 Predicted values versus the true values for random forests and gradient boosting models of regression

Boosting is an iterative procedure in which a set of weak learners produce a strong learner. At each step of boosting the weights on the data are modified by the results from a previous step. These methods have origins in classification problems and were later adapted to regression too. ²²² The outliers are better handled with the use of Huber loss criterion which has the following functional form,

$$L(y, f(x)) = \begin{cases} [y - f(x)]^2, & \text{for } |y - f(x)| \le \delta \\ \delta \left(|y - f(x)| - \frac{\delta}{2} \right), & \text{otherwise} \end{cases}$$

	Linear	Poly ridge	Random	Gradient
	regression	regression	forests	boost
Mean squared error	0.0056	0.1050	0.0014	0.0008
Variance score or R-squared	0.52	0.90	0.88	0.93

Table 6-3 Mean-squared error for the whole dataset with different models



The following chart shows the feature importance from random forests and gradient boost regression models. All the models are from the scikit-learn python library. ²²³



Figure 6-7 Feature importance for the selected 10 descriptors from random forests and gradient boosting models.

Since we have a small dataset we checked for overfitting with leave-one-out cross validation method wherein the model is trained on n-1 data points, n is the size of the dataset, and the

model performance on the remaining point is compared.

	Gradient	Gradient
	boosting – top	boosting – top 5
	10 descriptors	descriptors
Total combinations	26	26
Training set average MAE	0.0190	0.0190
Training set prediction accuracy within 2k _B T	100.00%	100%
Test set average MAE	0.0774	0.0681
Test set prediction accuracy within $2k_BT$	42.31%	50.00%
Test set prediction accuracy within 3k _B T	69.23%	65.38%

Table 6-4 Performance of Gradient boosting model when n-1 data points are used for training and tested on the remaining one point. Average mean absolute error for all the possible combinations is presented here and it is close to $3k_BT$.



With ten descriptors around 69% of Gradient boosting model's predictions lie within $3k_BT$ bounds. And with the top five descriptors average mean absolute error is 0.0681 for leave-one-out validation, and this is the best estimate we can obtain with this small dataset.

6.5 Prediction framework for new materials

The prediction accuracy of the model on unseen dataset needs to be improved with larger training sets and it is a time-consuming process. Pending addition of new training data, we used our current model to build a framework that goes till the end of predicting transport barriers. A set of 462 compounds of ABX₃ formula was generated from the following elements:

- A = ['Li', 'Be', 'Na', 'Mg', 'K', 'Ca', 'Rb', 'Pb', 'Sr', 'Cs', 'Ba', 'Al', 'Ga', 'In', 'Sn', 'Tl', 'Bi']
- B = ['Sc', 'Ti', 'V', 'Cr', 'Mn', 'Fe', 'Co', 'Ni', 'Cu', 'Zn', 'Y', 'Zr', 'Nb', 'Mo', 'Ru', 'Rh', 'Pd', 'Ag', 'Cd', 'La', 'Hf', 'Ta', 'W', 'Re', 'Os', 'Ir', 'Pt', 'Au', 'Hg']
- X = ['N', 'P', 'O', 'S', 'Se', 'F', 'Cl', 'Br', 'I']

The aflowlib ²⁰⁹ repository of materials data is queried for the 4,437 possible combinations but structural data was available only for 462 compounds and these included the 200 compounds screened before by Korbel, et al. ²⁰⁰ The structural data was needed to calculate the descriptors 'electron excitation energy (U^o)' and 'd_MO'. The top five attributes give a test set prediction accuracy of 65% within $3k_BT$ error bound and this model was chosen for its simplicity of calculating descriptors. With this model, predicting the electron transfer barriers resulted in values in the range [0.1, 0.22] for the whole set. The distribution of various elements in this input data is shown in the following graphs:





Figure 6-8 Distribution of elements in the input data for prediction. Estimation of ET barriers are between the element B and its neighbor in ABX₃.

The top 100 compounds with lower activation barriers are shown in Figure 6-8. These predictions are very rough estimates of the electron transfer barriers. To gain confidence in these results the inherent regression model still needs to be trained on a diverse set that involves lot of structural factors.



Figure 6-9 Estimations of activation barriers based on current model and top 100 compounds with lower barriers and potential good conductors.



Here are the graphs with all the 462 points plotted with the atomic numbers of elements in A, B and X with the electron transport barriers.



Figure 6-10 Elements in B Vs. A, and B Vs. X in ABX₃ and their predicted electron transfer barriers in eV.



It can be observed that third row transition metal compounds offer low barrier to the electron transfer as expected, since the electron is not bound as tightly as in the case of first row.

6.5 Conclusion

We started with a small test set of BMX₃ compounds and observed simple inferences related to the ligands. We later expanded to a larger set drawn from a mix of literature data and our own data. The top ten descriptors for electron transport can predict the actual values to a good accuracy. The only problem here is the lack of more computational data on electron transport. For the gradient boosted decision trees, the model 'predicted' very well the training data but the prediction on unseen data was not satisfactory. Larger data sets with structural and compositional similarity as well as directional anisotropy need to be generated to get a better prediction accuracy and for the emergence of more distinct patterns.



Chapter 7 Modeling ORR in CuS pertinent to Water splitting

7.1 Introduction

Water splitting is a fundamental reaction in photo-electrochemistry and heterogenous catalysts with complex properties are used to ramp up the kinetic rates. Density functional theory (DFT) has been at the forefront of understanding surface reactivity and giving a full picture of the thermodynamics accurately. DFT has been instrumental in deriving the design principles for several catalysts used in water splitting. ^{12, 224-228} One of the recent discoveries in photocatalysts are transitional metal sulfide (TMS) nanomaterials, which are proven to be effective for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).²²⁹⁻²³¹ ORR occurs at the cathode of polymer electrolyte membrane fuel cells and metal-air batteries and its rate strongly influences the performance of these devices.^{232, 233}

Platinum free ORR electrocatalysts using TMS nanocrystals (NCs) have potential advantages such as low cost, comparable electrochemical activity to precious metals, and tunable physical and chemical properties. Among TMS compounds Fe-S, Ni-S, and Co-S systems,²³⁴⁻²³⁷ are widely explored and recently copper sulfide [Cu_{2-x}S ($0 \le x \le 1$)] nanocrystals caught the interest of chemists.²³⁸⁻²⁴² Among the many crystal phases and compositions of Cu_{2-x}S, covellite CuS shows good electron mobility and free hole density, which are highly desired characteristics for electronic and catalytic applications.

Our experimental collaborators synthesized covellite CuS nano-platelets (NPls) of controllable lateral dimensions and we investigated theoretically how facet selectivity contributes to the anisotropic conductivity. DFT calculated oxygen adsorption energy diagrams for the ORR



on the three possible surface terminations (two types of (001) planes, and a (110) plane) are investigated here to compare with the experimental results.

7.2 Covellite structure

Covellite consists of layers of triangular CuS_3 units (denoted as Cu1), each sandwiched between two layers of CuS_4 tetrahedra (denoted as Cu2). Each triple layer is linked to the triple layers above and below it via disulfide bonds.



Figure 7-1. (a) Structural model of covellite CuS. Potential ORR surfaces: (b) (110) planes with mixed Cu1 and Cu2 atoms, (c) Cu2 terminated and (d) Cu1 terminated (001) planes. The arrows indicate cleavage planes that produce the two different (001) surfaces.

Here, the notations Cu1 and Cu2 indicate the chemical environment of copper atoms in bulk covellite, and their chemical properties will be different on an exposed (001) or (110) surface, due to the change of ligands and surface relaxation. For each covellite CuS unit cell, cleavage on (110) planes can lead to exposure of two Cu1 atoms and four Cu2 atoms, whereas (001) has



either Cu1 or Cu2 atom termination. The kinetically most favorable reaction pathway for the ORR process catalyzed by a nonprecious-metal catalyst in alkaline solution is a molecular oxygen associative or dissociative adsorption mechanism. In section 7.4 we will see in greater detail which of these two mechanisms is the most favorable and for which surface termination.

7.3 Calculation details

Calculations were done using spin-polarized density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) functional augmented with dispersion correction DFT-D3 of Grimme (with zero damping), using Vienna ab initio Simulation Package (VASP).²⁴³⁻²⁴⁷ Projected augmented wave (PAW) pseudopotentials were used for Cu (valence $3d^{10}4s^{1}$), S (valence $3s^{2}3p^{4}$), and O (valence $2s^{2}2p^{4}$) for the treatment of ion cores.^{248, 249} We used an energy cutoff of 400 eV for the plane wave basis set, along with a Gaussian-smearing width of $k_{B}T =$ 0.05 eV for partial occupancy of states near the Fermi level.

	ZPE	TS
* (site)	0.00	0.00
0*	0.05	0.00
OH*	0.35	0.00
OOH*	0.41	0.00
00*	0.10	0.00
H ₂ O	0.56	0.67
H ₂	0.27	0.41
¹ / ₂ O ₂	0.32	0.05
H ₂ O ₂	0.69	0.72

Table 7-1 Zero Point Energy Corrections and Entropic Contributions to the Free Energies We used a Monkhorst-Pack *k*-point grid generated using the methodology of Wisesa, *et al.*, to accelerate the calculations.²⁵⁰ We applied zero-point energy (ZPE), enthalpy (*S*), and entropy



corrections to reaction energies as proposed by Valdes *et al.*²⁵¹ and gathered in Table 7-1. We performed calculations of the oxygen reduction reaction on covellite CuS (001) and (110) surfaces as periodic slabs. Two CuS (001) slabs with two different terminations were defined (with surfaces marked Cu1 and Cu2 in Figure 8).²⁵² Each had a hexagonal surface cell with dimensions of 7.60 Å × 37.00 Å ($\gamma = 120.0^{\circ}$) and four copper atoms exposed on the surface. The CuS (110) slab had an orthorhombic surface cell with dimensions of 16.47 Å × 6.60 Å × 27.43 Å, and 6 copper atoms exposed at the surface. All slab models contained seven layers of ions, and a vacuum space of at least 14 Å to avoid interactions between surfaces and their periodic images. All systems were optimized with a force convergence criterion of 0.01 eV/Å while the bottom two layers were fixed.

7.4 DFT-Calculated Oxygen Adsorption Energy and Facet-Dependent ORR Behavior

We investigated the two possible reaction mechanisms previously suggested. In the dissociative mechanism, the O_2 molecules dissociate before they are hydrogenated, while in the associative mechanism they are hydrogenated before they dissociate. We referenced the step energies for each electrode half reaction to a standard hydrogen electrode (SHE) by replacing the energy of a proton-electron pair $E(H^+ + e^-)$ with the energy of a hydrogen molecule $E(H_2)$. This allows the results to be compared directly with the experimental results (E vs. RHE).

The associative mechanism proceeds via the adsorption of molecular O_2 followed by reduction: ²²⁸

- 1. $O_2 + * (site) + H^+ + e^- \rightarrow HOO^*$
- 2. HOO* + H⁺ + $e^- \rightarrow$ H₂O + O*



- 3. $O^* + H^+ + e^- \rightarrow HO^*$
- 4. $HO^* + H^+ + e^- \rightarrow H_2O + *$

The dissociative mechanism proceeds via O-O bond breaking followed by reduction:

- 5. $\frac{1}{2}O_2 + *(site) + H^+ + e^- \rightarrow HO^*$
- 6. $HO^* + H^+ + e^- \rightarrow H_2O + *$

Structures of the O₂ adsorption intermediate for the several slabs are shown in Figure 7-2. The



Figure 7-2 Optimized surface structures for intermediates in the ORR reaction and DFT study on different CuS surfaces. (a) O₂ adsorbed on the Cu1 terminated (001) surface, forming a peroxo bridge between two Cu atoms. (b) Dangling O₂ bound to the Cu2 terminated (001) surface. (c) Dangling O₂ bound to a Cu1 atom on the (110) surface with the Cu atom bound to two sulfur atoms. (d) Dangling O₂ bound to the Cu2 atom on the (110) surface with the Cu atom bound to two sulfur atoms.

energies are given in Table 7-2. The key energies are the "adsorption energies" defined as:

$$E(ads) = E(*-O_2) - E(*) - E(O_2)$$

for the associative mechanism;



E(ads) = E(ads)	(*-O) - E(*)	$-\frac{1}{2}E(O_2)$
-----------------	--------------	----------------------

for the dissociative mechanism.

Surface / active site	Mechanism		E(ads)
(001) Cu2	Dissociative O* adsorption		0.75
(001) Cu1	Dissociative	O* adsorption	1.52
(110) Cu1 site	Dissociative O* adsorption		1.03
(110) Cu2 site	Dissociative	O* adsorption	0.62
(001) Cu2	Associative	O ₂ adsorption	-0.26
(001) Cu1	Associative	O ₂ adsorption	0.42
(110) Cu1 site	Associative	O ₂ adsorption	-0.01
(110) Cu2 site	Associative O ₂ adsorption		0.52

Table 7-2 Oxygen molecule adsorption energies on different sites

Gibbs free energies were calculated as: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$. We used a standard hydrogen electrode (SHE) at pH=0, p = 1 bar, and T = 298.15 K as a reference. The free energy of the electron ($\Delta G[e^-]$) and proton ($\Delta G[H^+]$) are replaced with $\Delta G[H_2] + e U$, where U is the external potential versus SHE. To bypass the poor DFT description of the O₂ ground state molecule, the free energy of the di-oxygen molecule was calculated as

$$\Delta G[O_2] = 4.92 \text{ eV} + 2\Delta G[H_2O] - 2\Delta G[H_2]$$

The overpotential for the associative mechanism was determined as

$$OP = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4) + 1.23 \text{ eV}$$

where ΔG_1 , ΔG_2 , ΔG_3 , and ΔG_4 are the reaction free energies for steps (1), (2), (3), and (4) respectively. The overpotential for the dissociative mechanism was determined similarly as

$$OP = \max(\Delta G_5, \Delta G_6) + 1.23 \text{ eV}$$



Figure 7-2(a-d) illustrates the geometry and energy of adsorbed O_2 for the ORR intermediates on different surfaces of CuS NPIs. Oxygen adsorption, the rate-determining step of ORR, was more promoted on Cu2 terminated (001) planes than on those with Cu1 atom termination or on (110) planes with mixed Cu1 and Cu2 termination. The relative energy profile of the ORR



Figure 7-3 Reaction free energy diagrams for Cu1 terminated (001) surfaces (red), Cu2 terminated (001) surfaces (blue), and (110) surfaces (green). Both bridge-like and dangling O₂ adsorption mechanisms were applied to each CuS surface, and the stable surfaces are presented after surface relaxation. The oxygen adsorption energy on (110) surfaces was calculated separately on both Cu1 and Cu2 atoms.

process on each CuS surface was calculated, as shown in Figure 7-3. The detailed calculated adsorption energies are provided in Table 7-2.

For the (110) surfaces, the indicated adsorption energies correspond to the average value for Cu1 and Cu2 as active sites. The results show that adsorption of the oxygen molecule is preferred on the Cu2 site of the CuS (001) surface, with the lowest adsorption energy of -0.26 eV. Thus, the O₂ adsorption on Cu2 terminated (001) planes is exothermic. For the (110) surface, the computed adsorption energy of O₂ on Cu1 atoms is -0.012 eV.



In all other cases of associative or dissociative mechanisms, the first adsorption step is energetically unfavorable, with positive ΔE_{abs} . The step energies and overpotential for ORR associative and dissociative mechanisms are presented in Table 7-3. Compared with the (001)-Cu1 termination and side surfaces with mixed Cu1 and Cu2 sites, the overpotential for the associative mechanism at the (001)-Cu2 termination is found to be ~0.55 eV, in good agreement with the experiments. And the overall electrochemical process at Cu2 sites is more easily initiated. Therefore, DFT results support the conclusion that CuS NPls, particularly Cu2 terminated (001) planes, have an excellent potential for ORR.

	(001) Cu2	(001) Cu1	(110) Cu1 site	(110) Cu2 site
$1. O_2 + * (site) + H^+ + e^- = HOO^*$	-0.68	-0.10	-0.28	-0.48
2. HOO* + H ⁺ + e^- = H ₂ O + O*	-0.92	-0.84	-1.14	-1.36
3. $O^* + H^+ + e^- = HO^*$	-2.17	-1.70	-2.19	-1.88
4. $HO^* + H^+ + e^- = H_2O + *$	-1.15	-2.29	-1.31	-1.20
$5. \frac{1}{2}O2 + *(site) + H^+ + e^- = HO^*$	-1.31	-0.17	-1.16	-1.26
6. $HO^* + H^+ + e^- = H_2O + *$	-1.15	-2.29	-1.31	-1.20
Overpotential of associative mechanism	0.55	1.14	0.95	0.75
Overpotential of dissociative mechanism	0.08	1.06	0.08	0.02

Table 7-3 Step energy and overpotential for ORR associative and dissociative mechanisms.

7.5 Conclusion

DFT calculations show that the electrochemical activity for covellite CuS NPIs is anisotropic and highly facet-dependent, which is consistent with experimental observations. A four-electron associative mechanism of ORR is found to be the most favorable mechanism for the most reactive surface termination. The basal planes, in particular the Cu2 terminated (001) planes, possess lowest overall O₂ adsorption energy and thereby are more favorable to initiate ORR.



Although the overall ORR performance of the CuS NPIs does not yet match that of precious metal catalysts, we believe that our results provide new insights into facet-sensitive electrochemical reactions of 2D TMS nanomaterials, with well-defined morphologies, for electrochemical applications.



Chapter 8 Summary and Outlook

8.1 Conclusions

In this research work we focused on developing methods for the determination of carrier mobility in periodic crystalline systems with minimal approximations. Within Marcus-Holstein localized quasi-diabatic two-states model of polaron, our development that makes it possible to evaluate the atomistic parameters electronic coupling V_{AB} and the activation barrier ΔG by firstprinciples methods offers an effective way to estimate of the macroscopic conductivity. In the second chapter we reported a new implementation of the method, based on the corresponding orbital transformation.²⁵³ We carefully segregated the plane-waves and pseudopotentials based total energy term in CP2K into the one-electron, and two-electron energy contributions, which are needed for the evaluation of the off-diagonal term H_{AB} . We showed results for prototypical photocatalysts viz., bulk hematite Fe_2O_3 , bulk titanium dioxide TiO_2 , and bulk bismuth vanadate BiVO₄, etc., that highlight the capability of the new module that is embedded in the CP2K code. This new capability allows the complete characterization of electron transfer in the solid state with CP2K. Taking any localized single determinant wavefunction of the system from HF, DFT, hybrid DFT, DFT+U, or cDFT theory we can calculate VAB with a cost of one single iteration of an HF calculation. Object-oriented programming framework of CP2K allows to re-use several of the high-performance computing routines.

In the next chapter we showed how the 'maximal orbital analysis' method MOA is implemented for periodic solid-state calculations. MOA is a wavefunction characterization method that guarantees a maximal projection onto the atomic basis sets. This is a efficient measure of the electron population overlap between atoms or atomic fragments of interest. It can help in deciphering the mechanism of superexchange using an orbital picture. Test cases were



presented for bulk rutile TiO_2 , bulk Fe_2O_3 and a model system of 1D chain of iron (ferric) units. Excess electron orbital is successfully isolated in case of TiO_2 which gives a perfect underlying picture of charge distribution during ET with well-chosen atomic fragments. Many such systems can benefit from a quick analysis with MAO that captures overlap. It can be a very good metric to assess efficacy of ET among an array of test compounds.

In chapter four we show that metadynamics with collective coordinates defined to represent the bond elongation and compressions associated with a polaron transfer mechanism can accelerate hopping events. The methodology shows promise in estimating the activation barrier directly with short trajectories, and without any approximation beyond DFT. The only pitfall in this method is the need for a careful choice of hyperparameters, the biasing gaussian height, width and deposition rate. We found that the potential energy basins should not be flooded with the frequent deposition of biasing gaussian potentials and at the same time the gaussians being added should be narrow enough to not bring down the transition region. This is a conflicting objective and we believe that the parameters 'tuned' in our work for bulk TiO₂ may be a good starting point for other metal oxide semiconductors, as they exhibit similar vibrational density of states. Another issue we highlighted here is the need for an adaptive self-learning bias to stop adding bias over time and smoothly converge the free energy surface.

In the next chapter we tried to isolate the breathing mode involved in electron transfer using the vibrational spectrum of the atomic fragments involved in transfer. For this purpose, we evaluated the compressed sensing methodology against Fast Fourier Transform. Compressed sensing captures a sparse signal and our objective is to extract as many peaks as possible in the vibrational spectrum from as short as possible molecular dynamics trajectory. When compared to application of Fourier transform compressed sensing is not significantly better, as was the case



for molecules presented in Andrade et al. ¹⁵ There are huge number of coupled lattice vibrations in bulk systems that deter this method to be as effective as in the case of small molecules wherein peaks are a few and well separated.

In chapter 6 we discussed how Machine learning methods have gained dominance in materials discovery and design. ML models are as good as the training data and descriptors that are representative of the functionality we want to predict. We found good correlation between the electron excitation energy, ionic radius, cation-anion bond energies, cation-anion bond length, etc., and the overall transport behavior. Further work in this direction requires generation and curation of transport data to actively improve the model. Several tools such as atomate, and pymatgen interfaces offer a readymade solution to manage a high throughput setup. ^{254, 255}

In the next chapter we evaluated the electrochemical activity of covellite CuS nanoplatelets toward oxygen reduction (ORR) based on DFT calculations. We showed that anisotropy and facet-dependence in this system, features that agree with experimental observations. Cu2-type (001) basal plane terminations are the most reactive surface terminations. These planes possess lowest overall O₂ adsorption energy and thereby are more favorable to initiate ORR. A four-electron associative mechanism of ORR is found to be the most favorable mechanism for this surface. By combining experimental and computational methods we get a quantitative description of chemical processes at the solid-liquid interface. Facet-sensitive electrochemical reactions of 2D TMS nanomaterials, with well-defined morphologies are described in our work and this goes further in the design of new catalysts with similar ligands.

8.2 Outlook

In less than a decade in-silico materials discovery has reached new heights with the availability of new generation computers, community developed open source software tools and the



emergence of machine learning as a powerful predictive tool. Open science is instrumental in promoting transparency in scientific investigations, making data accessible and reusable. Now the focus is on extending the current descriptions to explain new chemistries and increasing familiarity to existing methods. Electron Transfer theory has spawned a wide variety of subtopics with active research into high impact applications. Whether it is semiconductor photocatalysts or photo-redox reactions in molecules, Marcus theory has established a thorough atomistic description. When we incorporate these finer details into our base calculations then we can enrich the predictive power of our machine learning models.


References

1. Togo, A.; Tanaka, I., First principles phonon calculations in materials science. *Scripta Materialia* **2015**, *108*, 1-5.

2. US/OSTP, Materials Genome Initiative for Global Competitiveness. *National Science and Technology Council, US Gov* **2011**.

3. US/OSTP, MGI Strategic plan. *Committee on Technology, US Gov* 2014.

4. de Pablo, J. J.; Jackson, N. E.; Webb, M. A.; Chen, L.-Q.; Moore, J. E.; Morgan, D.; Jacobs, R.; Pollock, T.; Schlom, D. G.; Toberer, E. S.; Analytis, J.; Dabo, I.; DeLongchamp, D. M.; Fiete, G. A.; Grason, G. M.; Hautier, G.; Mo, Y.; Rajan, K.; Reed, E. J.; Rodriguez, E.; Stevanovic, V.; Suntivich, J.; Thornton, K.; Zhao, J.-C., New frontiers for the materials genome initiative. *npj Computational Materials* **2019**, *5* (1).

5. Curtarolo, S.; Setyawan, W.; Hart, G. L. W.; Jahnatek, M.; Chepulskii, R. V.; Taylor, R. H.; Wanga, S.; Xue, J.; Yang, K.; Levy, O.; Mehl, M. J.; Stokes, H. T.; Demchenko, D. O.; Morgan, D., AFLOW: An automatic framework for high-throughput materials discovery. *Computational Materials Science* **2012**, *58*, 218-226.

6. Olivares-Amaya, R.; Amador-Bedolla, C.; Hachmann, J.; Atahan-Evrenk, S.; Sanchez-Carrera, R. S.; Vogt, L.; Aspuru-Guzik, A., Accelerated computational discovery of high-performance materials for organic photovoltaics by means of cheminformatics. *Energy & Environmental Science* **2011**, *4* (12), 4849-4861.

7. Talirz, L.; Kumbhar, S.; Passaro, E.; Yakutovich, A. V.; Granata, V.; Gargiulo, F.; Borelli, M.; Uhrin, M.; Huber, S. P.; Zoupanos, S.; Adorf, C. S.; Andersen, C. W.; Schütt, O.; Pignedoli, C. A.; Passerone, D.; VandeVondele, J.; Schulthess, T. C.; Smit, B.; Pizzi, G.; Marzari, N. Materials Cloud, a platform for open computational science *arXiv e-prints* [Online], 2020, p. arXiv:2003.12510. <u>https://ui.adsabs.harvard.edu/abs/2020arXiv200312510T</u> (accessed March 01, 2020).

8. Jain, A.; Shyue Ping, O.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A., Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *Apl Materials* **2013**, *1* (1).

9. Draxl, C.; Scheffler, M., NOMAD: The FAIR concept for big data-driven materials science. *MRS Bulletin* **2018**, *43* (9), 676-682.

10. Saal, J. E.; Kirklin, S.; Aykol, M.; Meredig, B.; Wolverton, C., Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD). *JOM* **2013**, *65* (11), 1501-1509.

11. Landis, D. D.; Hummelshøj, J. S.; Nestorov, S.; Greeley, J.; Dułak, M.; Bligaard, T.; Nørskov, J. K.; Jacobsen, K. W., The Computational Materials Repository. *Computing in Science & Engineering* **2012**, *14* (6), 51-57.

12. Nørskov, J. K.; Bligaard, T., The Catalyst Genome. *Angewandte Chemie International Edition* **2013**, *52* (3), 776-777.

13. Quadrennial Technology Review. *Department of Energy*, <u>https://www.energy.gov/quadrennial-technology-review-0</u> 2015.



126

14. King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G., Corresponding Orbitals and the Nonorthogonality Problem in Molecular Quantum Mechanics. *The Journal of Chemical Physics* **1967**, *47* (6), 1936-1941.

15. Andrade, X.; Sanders, J. N.; Aspuru-Guzik, A., Application of compressed sensing to the simulation of atomic systems. *Proceedings of the National Academy of Sciences* **2012**, *109* (35), 13928-13933.

16. Hautier, G.; Miglio, A.; Ceder, G.; Rignanese, G. M.; Gonze, X., Identification and design principles of low hole effective mass p-type transparent conducting oxides. *Nature Communications* **2013**, *4*.

17. Hautier, G.; Miglio, A.; Waroquiers, D.; Rignanese, G.-M.; Gonze, X., How Does Chemistry Influence Electron Effective Mass in Oxides? A High-Throughput Computational Analysis. *Chemistry of Materials* **2014**, *26* (19), 5447-5458.

18. Rosso, K. M.; Smith, D. M. A.; Dupuis, M., An ab initio model of electron transport in hematite (alpha-Fe2O3) basal planes. *Journal of Chemical Physics* **2003**, *118* (14), 6455-6466.

19. Hush, N. S.; Vlcek, A. A.; Stranks, D. R.; Marcus, R. A.; Weiss, J.; Bell, R. P.; Halpern, J.; Orgel, L. E.; Adamson, A. W.; Dainton, F. S.; Williams, R. J. P.; Taube, H.; Shimi, I. A. W.; Higginson, W. C. E.; Stead, J. B.; Waind, G. M.; Rosseinsky, D. R.; Wells, C. F.; Sutcliffe, L. H.; Proll, P. J.; King, E. L.; Stranks, D. R.; Pearson, R. G.; Basolo, F.; Poe, A. J.; Fordsmith, M. H.; Sutin, N.; Dodson, R. W.; Baughan, C., Exchange reactions and electron transfer reactions including isotopic exchange - general discussion. *Discussions of the Faraday Society* **1960**, (29), 113-136.

20. Marcus, R. A., Theory of oxidation-reduction reactions involving electron transfer .4. A statistical-mechanical basis for treating contributions from solvent, ligands, and inert salt. *Discussions of the Faraday Society* **1960**, (29), 21-31.

21. Marcus, R. A., Chemical + electrochemical electron-transfer theory. *Annual Review of Physical Chemistry* **1964**, *15*, 155-196.

22. Marcus, R. A., On theory of electron-transfer reactions .6. Unified treatment for homogeneous and electrode reactions. *Journal of Chemical Physics* **1965**, *43* (2), 679.

23. Marcus, R. A., Electron transfer at electrodes and in solution - comparison of theory and experiment. *Electrochimica Acta* **1968**, *13* (5), 995-&.

24. Marcus, R. A.; Siders, P., Further developments in electron-transfer. *Acs Symposium Series* **1982**, *198*, 235-253.

25. Marcus, R. A.; Sutin, N., Electron Transfers in Chemistry and Biology. *Biochimica Et Biophysica Acta* **1985**, *811* (3), 265-322.

26. Marcus, R. A., Electron-transfer reactions in chemistry - Theory and experiment. *Reviews of Modern Physics* **1993**, *65* (3), 599-610.

27. Warshel, A., Dynamics of reactions in polar-solvents - semi-classical trajectory studies of electron-transfer and proton-transfer reactions. *Journal of Physical Chemistry* **1982**, *86* (12), 2218-2224.

28. Hwang, J. K.; Warshel, A., Microscopic examination of free-energy relationships for electron-transfer in polar-solvents. *Journal of the American Chemical Society* **1987**, *109* (3), 715-720.

29. King, G.; Warshel, A., Investigation of the free-energy functions for electron-transfer reactions. *Journal of Chemical Physics* **1990**, *93* (12), 8682-8692.



127

30. Kuharski, R. A.; Bader, J. S.; Chandler, D.; Sprik, M.; Klein, M. L.; Impey, R. W., Molecular-model for aqueous ferrous ferric electron-transfer. *Journal of Chemical Physics* **1988**, *89* (5), 3248-3257.

31. Logan, J.; Newton, M. D., Abinitio study of electronic coupling in the aqueous Fe-2+-Fe-3+ electron exchange process. *Journal of Chemical Physics* **1983**, 78 (6), 4086-4091.

32. Newton, M. D.; Sutin, N., Electron-transfer reactions in condensed phases. *Annual Review of Physical Chemistry* **1984**, *35*, 437-480.

33. Newton, M. D., Electronic-structure analysis of electron-transfer matrix-elements for transition-metal redox pairs. *Journal of Physical Chemistry* **1988**, *92* (11), 3049-3056.

34. Blumberger, J.; Sprik, M., Free energy of oxidation of metal aqua ions by an enforced change of coordination. *Journal of Physical Chemistry B* **2004**, *108* (21), 6529-6535.

35. Blumberger, J.; Sprik, M., Ab initio molecular dynamics simulation of the aqueous Ru2+/Ru3+ redox reaction: The Marcus perspective. *Journal of Physical Chemistry B* **2005**, *109* (14), 6793-6804.

36. Blumberger, J.; Sprik, M., Quantum versus classical electron transfer energy as reaction coordinate for the aqueous Ru2+/Ru3+ redox reaction. *Theoretical Chemistry Accounts* **2006**, *115* (2-3), 113-126.

37. Barbara, P. F.; Meyer, T. J.; Ratner, M. A., Contemporary Issues in Electron Transfer Research. *The Journal of Physical Chemistry* **1996**, *100* (31), 13148-13168.

38. Blumberger, J., Recent Advances in the Theory and Molecular Simulation of Biological Electron Transfer Reactions. *Chemical Reviews* **2015**, *115* (20), 11191-11238.

39. Beratan, D. N.; Skourtis, S. S.; Balabin, I. A.; Balaeff, A.; Keinan, S.; Venkatramani, R.; Xiao, D. Q., Steering Electrons on Moving Pathways. *Accounts of Chemical Research* **2009**, *42* (10), 1669-1678.

40. Beratan, D. N., Why Are DNA and Protein Electron Transfer So Different? In *Annual Review of Physical Chemistry, Vol 70*, Johnson, M. A.; Martinez, T. J., Eds. 2019; Vol. 70, pp 71-97.

41. Friedman, L.; Holstein, T., Studies of polaron motion .3. the hall mobility of the small polaron. *Annals of Physics* **1963**, *21* (3), 494-549.

42. Emin, D.; Holstein, T., Adiabatic Theory of Hall Mobility of Small Polaron in Hopping Regime. *Bulletin of the American Physical Society* **1968**, *13* (3), 464.

43. Emin, D.; Holstein, T., Studies of Small Polaron Motion. 4. Adiabatic Theory of Hall Effects. *Annals of Physics* **1969**, *53* (3), 439-520.

44. Austin, I. G.; Mott, N. F., Polarons in crystalline and non-crystalline materials. *Advances in Physics* **1969**, *18* (71), 41-102.

45. Emin, D., Correlated small-polaron hopping motion. *Physical Review Letters* **1970**, *25* (26), 1751-1755.

46. Emin, D., Lattice Relaxation and Small-Polaron Hopping Motion. *Physical Review B* **1971**, *4* (10), 3639-3651.

47. Emin, D., Phonon-assisted transition rates .1. optical-phonon-assisted hopping in solids. *Advances in Physics* **1975**, *24* (3), 305-348.

48. Emin, D., Transport properties of small polarons. *Journal of Solid State Chemistry* **1975**, *12* (3-4), 246-252.

49. Iordanova, N.; Dupuis, M.; Rosso, K. M., Charge transport in metal oxides: A theoretical study of hematite alpha-Fe2O3. *Journal of Chemical Physics* **2005**, *122* (14), 144305.



50. Deskins, N. A.; Dupuis, M., Electron transport via polaron hopping in bulk TiO2: A density functional theory characterization. *Physical Review B* **2007**, *75*, 195212-195221.

51. Deskins, N. A.; Rao, P. M.; Dupuis, M., Charge carrier management in semiconductors: mdodelng charge transport and recombination. *Springer Handbook of Inorganic Photochemistry* **2019**.

52. Oberhofer, H.; Reuter, K.; Blumberger, J., Charge Transport in Molecular Materials: An Assessment of Computational Methods. *Chemical Reviews* **2017**, *117* (15), 10319-10357.

53. Shirakawa, H.; Louis, E. J.; Macdiarmid, A. G.; Chiang, C. K.; Heeger, A. J., Synthesis of electrically conducting organic polymers - halogen derivatives of polyacetylene, (CH)x. *Journal of the Chemical Society-Chemical Communications* **1977**, (16), 578-580.

54. Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; Macdiarmid, A. G., Electrical-conductivity in doped polyacetylene. *Physical Review Letters* **1977**, *39* (17), 1098-1101.

55. Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Macdiarmid, A. G., Conducting polymers - halogen doped polyacetylene. *Journal of Chemical Physics* **1978**, *69* (11), 5098-5104.

56. Ikehata, S.; Kaufer, J.; Woerner, T.; Pron, A.; Druy, M. A.; Sivak, A.; Heeger, A. J.; Macdiarmid, A. G., Solitons in polyacetylene - magnetic-susceptibility. *Physical Review Letters* **1980**, *45* (13), 1123-1126.

57. Park, Y. W.; Heeger, A. J.; Druy, M. A.; Macdiarmid, A. G., Electrical transport in doped polyacetylene. *Journal of Chemical Physics* **1980**, *73* (2), 946-957.

58. Chen, S. N.; Heeger, A. J.; Kiss, Z.; Macdiarmid, A. G.; Gau, S. C.; Peebles, D. L., Polyacetylene, (CH)x - photoelectrochemical solar-cell. *Applied Physics Letters* **1980**, *36* (1), 96-98.

59. Etemad, S.; Mitani, T.; Ozaki, M.; Chung, T. C.; Heeger, A. J.; Macdiarmid, A. G., Photoconductivity in polyacetylene. *Solid State Communications* **1981**, *40* (1), 75-79.

60. Heeger, A. J.; Macdiarmid, A. G., Transport, magnetic and structural studies of polyacetylene. *Molecular Crystals and Liquid Crystals* **1981**, 77 (1-4), 1-24.

61. Moses, D.; Chen, J.; Denenstein, A.; Kaveh, M.; Chung, T. C.; Heeger, A. J.; Macdiarmid, A. G.; Park, Y. W., Inter-soliton electron hopping transport in trans-(CH)x. *Solid State Communications* **1981**, *40* (11), 1007-1010.

62. Su, W. P.; Schrieffer, J. R.; Heeger, A. J., Solitons in polyacetylene. *Physical Review Letters* **1979**, *42* (25), 1698-1701.

63. Su, W. P.; Schrieffer, J. R.; Heeger, A. J., Soliton excitations in polyacetylene. *Physical Review B* **1980**, *22* (4), 2099-2111.

64. Bredas, J. L.; Chance, R. R.; Silbey, R., Theoretical-studies of charged defect states in doped polyacetylene and polyparaphenylene. *Molecular Crystals and Liquid Crystals* **1981**, 77 (1-4), 319-332.

65. Bredas, J. L.; Street, G. B., Polarons, Bipolarons, and Solitons in Conducting Polymers. *Accounts of Chemical Research* **1985**, *18* (10), 309-315.

66. Bredas, J. L.; Calbert, J. P.; da Silva, D. A.; Cornil, J., Organic semiconductors: A theoretical characterization of the basic parameters governing charge transport. *Proceedings of the National Academy of Sciences of the United States of America* **2002**, *99* (9), 5804-5809.

67. Bredas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J., Charge-transfer and energy-transfer processes in pi-conjugated oligomers and polymers: A molecular picture. *Chemical Reviews* **2004**, *104* (11), 4971-5003.



68. Coropceanu, V.; Cornil, J.; da Silva, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L., Charge transport in organic semiconductors. *Chemical Reviews* **2007**, *107* (4), 926-952.

69. Bredas, J. L.; Norton, J. E.; Cornil, J.; Coropceanu, V., Molecular Understanding of Organic Solar Cells: The Challenges. *Accounts of Chemical Research* 2009, *42* (11), 1691-1699.
70. Kippelen, B.; Bredas, J. L., Organic photovoltaics. *Energy & Environmental Science* 2009, *2* (3), 251-261.

71. Korzdorfer, T.; Bredas, J. L., Organic Electronic Materials: Recent Advances in the DFT Description of the Ground and Excited States Using Tuned Range-Separated Hybrid Functionals. *Accounts of Chemical Research* **2014**, *47* (11), 3284-3291.

72. Rosso, K. M.; Dupuis, M., On charge transport in iron oxides. *Geochimica Et Cosmochimica Acta* **2005**, *69* (10), A778-A778.

73. Kerisit, S.; Rosso, K. M., Kinetic Monte Carlo model of charge transport in hematite (alpha-Fe2O3). *Journal of Chemical Physics* **2007**, *127* (12), 124706-124715.

74. Skomurski, F. N.; Kerisit, S.; Rosso, K. M., Structure, charge distribution, and electron hopping dynamics in magnetite (Fe3O4) (100) surfaces from first principles. *Geochimica Et Cosmochimica Acta* **2010**, *74* (15), 4234-4248.

75. Katz, J. E.; Zhang, X. Y.; Attenkofer, K.; Chapman, K. W.; Frandsen, C.; Zarzycki, P.; Rosso, K. M.; Falcone, R. W.; Waychunas, G. A.; Gilbert, B., Electron Small Polarons and Their Mobility in Iron (Oxyhydr)oxide Nanoparticles. *Science* **2012**, *337* (6099), 1200-1203.

76. Yu, J. G.; Rosso, K. M.; Bruemmer, S. M., Charge and Ion Transport in NiO and Aspects of Ni Oxidation from First Principles. *Journal of Physical Chemistry C* **2012**, *116* (2), 1948-1954.

77. Alexandrov, V.; Rosso, K. M., Electron transport in pure and substituted iron oxyhydroxides by small-polaron migration. *Journal of Chemical Physics* **2014**, *140* (23), 234701-234708.

78. Alexandrov, V.; Rosso, K. M., Ab initio modeling of Fe(II) adsorption and interfacial electron transfer at goethite (alpha-FeOOH) surfaces. *Physical Chemistry Chemical Physics* **2015**, *17* (22), 14518-14531.

79. Chatman, S.; Zarzycki, P.; Rosso, K. M., Spontaneous Water Oxidation at Hematite (alpha-Fe2O3) Crystal Faces. *Acs Applied Materials & Interfaces* **2015**, *7* (3), 1550-1559.

80. Kerisit, S.; Zarzycki, P.; Rosso, K. M., Computational Molecular Simulation of the Oxidative Adsorption of Ferrous Iron at the Hematite (001)-Water Interface. *Journal of Physical Chemistry C* **2015**, *119* (17), 9242-9252.

81. Zarzycki, P.; Kerisit, S.; Rosso, K. M., Molecular Dynamics Study of Fe(II) Adsorption, Electron Exchange, and Mobility at Goethite (alpha-FeOOH) Surfaces. *Journal of Physical Chemistry C* **2015**, *119* (6), 3111-3123.

82. Deskins, N. A.; Dupuis, M., Intrinsic Hole Migration Rates in TiO2 from Density Functional Theory. *Journal of Physical Chemistry C* **2009**, *113*, 346-358.

83. Morbec, J. M.; Galli, G., Charge transport properties of bulk Ta3N5from first principles. *Physical Review B* **2016**, *93* (3), 035201-035206.

Plata, J. J.; Marquez, A. M.; Sanz, J. F., Electron Mobility via Polaron Hopping in Bulk Ceria: A First-Principles Study. *Journal of Physical Chemistry C* 2013, *117* (28), 14502-14509.
Liu, T.; Pasumarthi, V.; LaPorte, C.; Feng, Z.; Li, Q.; Yang, J.; Li, C.; Dupuis, M., Bimodal hole transport in bulk BiVO4 from computation. *Journal of Materials Chemistry* 2018, 6, 3714-3723.



130

86. Pasumarthi, V.; Liu, T.; Dupuis, M.; Li, C., Charge carrier transport dynamics in W/Modoped BiVO4 : first principles-based mesoscale characterization. *Journal of Materials Chemistry A.* **2019**, *7*, 3054-3065.

87. Liao, P. L.; Carter, E. A., Optical Excitations in Hematite (alpha-Fe2O3) via Embedded Cluster Models: A CASPT2 Study. *Journal of Physical Chemistry C* **2011**, *115* (42), 20795-20805.

88. Liao, P. L.; Toroker, M. C.; Carter, E. A., Electron Transport in Pure and Doped Hematite. *Nano Letters* **2011**, *11* (4), 1775-1781.

89. Toroker, M. C.; Carter, E. A., Hole Transport in Nonstoichiometric and Doped Wustite. *Journal of Physical Chemistry C* **2012**, *116* (33), 17403-17413.

90. Kanan, D. K.; Carter, E. A., Ab initio study of electron and hole transport in pure and doped MnO and MnO:ZnO alloy. *Journal of Materials Chemistry A* **2013**, *1* (32), 9246-9256.

91. Iordanova, N.; Dupuis, M.; Rosso, K. M., Theoretical characterization of charge transport in chromia (alpha-Cr2O3). *J Chem Phys* **2005**, *123* (7), 074710.

92. Iordanova, N.; Dupuis, M.; Rosso, K. M., Charge transport in metal oxides: a theoretical study of hematite alpha-Fe2O3. *J Chem Phys* **2005**, *122* (14), 144305.

93. Deskins, N. A.; Dupuis, M., Electron transport via polaron hopping in bulkTiO2: A density functional theory characterization. *Physical Review B* **2007**, *75* (19).

94. Newton, M. D., Formalisms for electron-exchange kinetics in aqueous solution and the role of ab initio technqiues in their implementation. *International Journal of Quantum Chemistry* **1980**, *17*, 363-391.

95. Leontyev, I. V.; Basilevsky, M. V.; Newton, M. D., Theory and computation of electron transfer reorganization energies with continuum and molecular solvent models. *Theoretical Chemistry Accounts* **2004**, *111* (2-6), 110-121.

96. Cave, R. J.; Newton, M. D., Generalization of the Mulliken-Hush treatment for the calculation of electron transfer matrix elements. *Chemical Physics Letters* **1996**, *249* (1-2), 15-19.

97. Cave, R. J.; Newton, M. D., Calculation of electronic coupling matrix elements for ground and excited state electron transfer reactions: Comparison of the generalized Mulliken-Hush and block diagonalization methods. *Journal of Chemical Physics* **1997**, *106* (22), 9213-9226.

98. Cave, R. J.; Newton, M. D., Multistate Treatments of the Electronic Coupling in Donor-Bridge-Acceptor Systems: Insights and Caveats from a Simple Model. *Journal of Physical Chemistry A* **2014**, *118* (35), 7221-7234.

99. Cave, R. J.; Edwards, S. T.; Kouzelos, J. A.; Newton, M. D., Reduced Electronic Spaces for Modeling Donor/Acceptor Interactions. *Journal of Physical Chemistry B* **2010**, *114* (45), 14631-14641.

100. Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J., Stereoelectronic effects in intramolecular long-distance electron-transfer in radical-anions as predicted by *ab initio* MO calculations. *Journal of the American Chemical Society* **1986**, *108* (6), 1319-1320.

101. Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A., Electric-Field Induced Intramolecular Electron Transfer in Spiro pi-Electron Systems and Their Suitability as Molecular Electronic Devices - A Theoretical Study. *Journal of the American Chemical Society* **1990**, *112* (11), 4206-4214.



102. Jordan, K. D.; Paddonrow, M. N., Analysis of the interactions responsible for long-range through-bond-mediated electronic coupling between remote chromophores attached to rigid polynorbornyl bridges. *Chemical Reviews* **1992**, *92* (3), 395-410.

103. Shephard, M. J.; Paddonrow, M. N.; Jordan, K. D., Electronic coupling through saturated-hydrocarbon bridges. *Chemical Physics* **1993**, *176* (2-3), 289-304.

104. Paddon-Row, M. N., Investigating lang-range electron transfer processes with rigid, covalently linked donor-(norbornylogous bridge)-acceptor systems. *Accounts of Chemical Research* **1994**, *27*, 18-25.

105. Hohenberg, P.; Kohn, W., Inhomogeneous electron gas. *Physical Reviews* **1964**, *136*, B864-B871.

106. Kohn, W.; Sham, L. J., Self-consistent equations including exchange and correlation effects. *Physical Review* **1965**, *140* (4A), 1133-&.

107. Kaduk, B.; Kowalczyk, T.; Van Voorhis, T., Constrained Density Functional Theory. *Chemical Reviews* **2012**, *112* (1), 321-370.

108. Wu, Q.; Van Voorhis, T., Constrained density functional theory and its application in long-range electron transfer. *Journal of Chemical Theory and Computation* 2006, *2* (3), 765-774.
109. Wu, Q.; Van Voorhis, T., Extracting electron transfer coupling elements from constrained density functional theory. *Journal of Chemical Physics* 2006, *125* (16).

110. Ding, F. Z.; Wang, H. B.; Wu, Q.; Van Voorhis, T.; Chen, S. W.; Konopelski, J. P., Computational Study of Bridge-Assisted Intervalence Electron Transfer. *Journal of Physical Chemistry A* **2010**, *114* (19), 6039-6046.

111. Difley, S.; Van Voorhis, T., Exciton/Charge-Transfer Electronic Couplings in Organic Semiconductors. *Journal of Chemical Theory and Computation* **2011**, *7* (3), 594-601.

112. Goldey, M. B.; Brawand, N. P.; Voros, M.; Galli, G., Charge Transport in Nanostructured Materials: Implementation and Verification of Constrained Density Functional Theory. *Journal of Chemical Theory and Computation* **2017**, *13* (6), 2581-2590.

113. Futera, Z.; Blumberger, J., Electronic Couplings for Charge Transfer across Molecule/Metal and Molecule/Semiconductor Interfaces: Performance of the Projector Operator-Based Diabatization Approach. *Journal of Physical Chemistry C* **2017**, *121* (36), 19677-19689.

114. Gillet, N.; Berstis, L.; Wu, X. J.; Gajdos, F.; Heck, A.; de la Lande, A.; Blumberger, J.; Elstner, M., Electronic Coupling Calculations for Bridge-Mediated Charge Transfer Using Constrained Density Functional Theory (CDFT) and Effective Hamiltonian Approaches at the Density Functional Theory (DFT) and Fragment-Orbital Density Functional Tight Binding (FODFTB) Level. *Journal of Chemical Theory and Computation* **2016**, *12* (10), 4793-4805.

115. Kubas, A.; Gajdos, F.; Heck, A.; Oberhofer, H.; Elstner, M.; Blumberger, J., Electronic couplings for molecular charge transfer: benchmarking CDFT, FODFT and FODFTB against high-level ab initio calculations. II. *Physical Chemistry Chemical Physics* **2015**, *17* (22), 14342-14354.

116. Kubas, A.; Hoffmann, F.; Heck, A.; Oberhofer, H.; Elstner, M.; Blumberger, J., Electronic couplings for molecular charge transfer: Benchmarking CDFT, FODFT, and FODFTB against high-level ab initio calculations. *Journal of Chemical Physics* **2014**, *140* (10). 117. Manna, D.; Blumberger, J.; Martin, J. M. L.; Kronik, L., Prediction of electronic couplings for molecular charge transfer using optimally tuned range-separated hybrid functionals. *Molecular Physics* **2018**, *116* (19-20), 2497-2505.



118. Oberhofer, H.; Blumberger, J., Charge constrained density functional molecular dynamics for simulation of condensed phase electron transfer reactions. *Journal of Chemical Physics* **2009**, *131* (6).

119. Oberhofer, H.; Blumberger, J., Electronic coupling matrix elements from charge constrained density functional theory calculations using a plane wave basis set. *Journal of Chemical Physics* **2010**, *133* (24).

120. Spencer, J.; Gajdos, F.; Blumberger, J., FOB-SH: Fragment orbital-based surface hopping for charge carrier transport in organic and biological molecules and materials. *Journal of Chemical Physics* **2016**, *145* (6).

121. Lany, S.; Zunger, A., Polaronic hole localization and multiple hole binding of acceptors in oxide wide-gap semiconductors. *Physical Review B* **2009**, *80* (8), 085202.

122. Heyd, J.; Scuseria, G. E.; Ernzerhof, M., Hybrid functionals based on a screened Coulomb potential (vol 118, pg 8207, 2003). *Journal of Chemical Physics* **2006**, *124* (21).

123. Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P., Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Physical Review B* **1998**, *57* (3), 1505-1509.

124. Anisimov, V. I.; Zaanen, J.; Andersen, O. K., Band theory and Mott insulators - Hubbard-U instead of Stoner-1. *Physical Review B* **1991**, *44* (3), 943-954.

125. King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G., Corresponding Orbitals and Nonorthogonality Problem in Molecular Quantum Mechanics. *Journal of Chemical Physics* **1967**, *47* (6), 1936-1941.

126. Bylaska, E. J.; Rosso, K., Corresponding Orbitals Derived from Periodic Bloch States for Electron Transfer Calculations of Transition Metal Oxides. *Journal of Chemical Theory and Computation* **2018**, *14* (8), 4416-4426.

127. Rettie, A. J. E.; Chemelewski, W. D.; Emin, D.; Mullins, C. B., Unravelling Small-Polaron Transport in Metal Oxide Photoelectrodes. *Journal of Physical Chemistry Letters* **2016**, 7 (3), 471-479.

128. Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N., A semi-classical treatment of electron-exchange reactions - application to the hexaaquoiron(ii)-hexaaquoiron(iii) system. *Journal of the American Chemical Society* **1980**, *102* (18), 5798-5809.

129. Kestner, N. R.; Logan, J.; Jortner, J., Thermal electron-transfer reactions in polarsolvents. *Journal of Physical Chemistry* **1974**, *78* (21), 2148-2166.

130. Newton, M. D., Formalisms for electron-exchange kinetics in aqueous-solution and the role of *ab initio* techniques in their implementation. *International Journal of Quantum Chemistry* **1980**, *17*, 363-391.

131. Rosso, K. M.; Dupuis, M., Electron transfer in environmental systems: a frontier for theoretical chemistry. *Theoretical Chemistry Accounts* **2006**, *116* (1-3), 124-136.

132. Lowdin, P. O., Quantum theory of many-particle systems .1. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. *Physical Review* **1955**, *97* (6), 1474-1489.

133. Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J., cp2k: atomistic simulations of condensed matter systems. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2014**, *4* (1), 15-25.

134. Lippert, G.; Hutter, J.; Parrinello, M., The Gaussian and augmented-plane-wave density functional method for ab initio molecular dynamics simulations. *Theoretical Chemistry Accounts* **1999**, *103* (2), 124-140.



135. Lippert, G.; Hutter, J.; Parrinello, M., A hybrid Gaussian and plane wave density functional scheme. *Molecular Physics* **1997**, *92* (3), 477-487.

136. VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J., Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* **2005**, *167* (2), 103-128.

137. Guidon, M.; Hutter, J.; VandeVondele, J., Robust Periodic Hartree-Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets. *Journal of Chemical Theory and Computation* **2009**, *5* (11), 3010-3021.

138. Guidon, M.; Hutter, J.; VandeVondele, J., Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations. *J Chem Theory Comput* **2010**, *6* (8), 2348-64.

139. Krack, M.; Parrinello, M., All-electron ab-initio molecular dynamics. *Physical Chemistry Chemical Physics* **2000**, *2* (10), 2105-2112.

140. Schütt, O.; Messmer, P.; Hutter, J.; VandeVondele, J., GPU-Accelerated Sparse Matrix-Matrix Multiplication for Linear Scaling Density Functional Theory. In *Electronic Structure Calculations on Graphics Processing Units*, 2016; pp 173-190.

141. Borštnik, U.; VandeVondele, J.; Weber, V.; Hutter, J., Sparse matrix multiplication: The distributed block-compressed sparse row library. *Parallel Computing* 2014, *40* (5-6), 47-58.
142. Frigo, M.; Johnson, S. G., The Design and Implementation of FFTW3. *Proceedings of the IEEE* 2005, *93* (2), 216-231.

143. Guidon, M.; Schiffmann, F.; Hutter, J.; VandeVondele, J., Ab initio molecular dynamics using hybrid density functionals. *J Chem Phys* **2008**, *128* (21), 214104.

144. Dupuis, M.; Watts, J. D.; Villar, H. O.; Hurst, G. J. B., The general atomic and molecular electronic structure system hondo: Version 7.0. *Computer Physics Communications* **1989**, *52* (3), 415-425.

145. Guidon, M.; Hutter, J.; VandeVondele, J., Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations. *Journal of Chemical Theory and Computation* **2010**, *6* (8), 2348-2364.

146. Paier, J.; Hirschl, R.; Marsman, M.; Kresse, G., The Perdew-Burke-Ernzerhof exchange-correlation functional applied to the G2-1 test set using a plane-wave basis set. *Journal of Chemical Physics* **2005**, *122* (23).

147. Lowdin, P. O., Band theory, valence bond, and tight-binding calculations. *Journal of Applied Physics* **1962**, *33* (1), 251-+.

148. Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J., CP2K: atomistic simulations of condensed matter systems. *Wiley Interdisciplinary Reviews-Computational Molecular Science* **2014**, *4* (1), 15-25.

149. Humphrey, W.; Dalke, A.; Schulten, K., VMD: Visual molecular dynamics. *Journal of Molecular Graphics* **1996**, *14* (1), 33-38.

150. VandeVondele, J.; Hutter, J., Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J Chem Phys* **2007**, *127* (11), 114105.

151. Goedecker, S.; Teter, M.; Hutter, J., Separable dual-space Gaussian pseudopotentials. *Phys Rev B Condens Matter* **1996**, *54* (3), 1703-1710.

152. Hartwigsen, C.; Goedecker, S.; Hutter, J., Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. *Physical Review B* **1998**, *58* (7), 3641-3662.

153. Zijlstra, E. S.; Huntemann, N.; Kalitsov, A.; Garcia, M. E.; von Barth, U., Optimized Gaussian basis sets for Goedecker–Teter–Hutter pseudopotentials. *Modelling and Simulation in Materials Science and Engineering* **2009**, *17* (1), 015009.



154. Rosso, K. M.; Dupuis, M., Reorganization energy associated with small polaron mobility in iron oxide. *J Chem Phys* **2004**, *120* (15), 7050-4.

155. Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A* **1988**, *38* (6), 3098-3100.

156. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B* **1988**, *37* (2), 785-789.

157. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77* (18), 3865-3868.

158. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made

Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Physical Review Letters* **1997**, 78 (7), 1396-1396. 159. Marcus, R. A.; Sutin, N., Electron transfers in chemistry and biology. *Biochimica et Biophysica Acta (BBA) - Reviews on Bioenergetics* **1985**, *811* (3), 265-322.

160. Mizokawa, T.; Fujimori, A., Description of Spin and Charge Domain Walls in Doped Perovskite-Type3dTransition-Metal Oxides Based on Superexchange Interaction. *Physical Review Letters* **1998**, *80* (6), 1320-1323.

161. Szabo, A.; Ostlund, N. S., *Modern quantum chemistry : introduction to advanced electronic structure theory*. 1982.

162. Dupuis, M.; Nallapu, M., Maximal orbital analysis of molecular wavefunctions. *J Comput Chem* **2019**, *40* (1), 39-50.

163. Kühne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F.; Golze, D.; Wilhelm, J.; Chulkov, S.; Bani-Hashemian, M. H.; Weber, V.; Borstnik, U.; Taillefumier, M.; Shoshana Jakobovits, A.; Lazzaro, A.; Pabst, H.; Müller, T.; Schade, R.; Guidon, M.; Andermatt, S.; Holmberg, N.; Schenter, G. K.; Hehn, A.; Bussy, A.; Belleflamme, F.; Tabacchi, G.; Glöß, A.; Lass, M.; Bethune, I.; Mundy, C. J.; Plessl, C.; Watkins, M.; VandeVondele, J.; Krack, M.; Hutter, J. CP2K: An Electronic Structure and Molecular Dynamics Software Package -- Quickstep: Efficient and Accurate Electronic Structure Calculations *arXiv e-prints* [Online], 2020, p. arXiv:2003.03868. <u>https://ui.adsabs.harvard.edu/abs/2020arXiv200303868K</u> (accessed March 01, 2020).

164. Iannuzzi, M.; Chassaing, T.; Wallman, T.; Hutter, J., Ground and excited state density functional calculations with the Gaussian and augmented-plane-wave method. *CHIMIA International Journal for Chemistry* **2005**, *59* (7), 499-503.

165. VandeVondele, J.; Hutter, J. r., An efficient orbital transformation method for electronic structure calculations. *The Journal of Chemical Physics* **2003**, *118* (10), 4365.

166. M. Dupuis, J. D. W., H.O. Villar, HONDO7. In *Quantum Chemistry Program Exchange*, 1988; p 544.

167. M. Dupuis, J. R., H.F. King, HONDO. In *Quantum Chemistry Program Exchange*, 1977; pp 336,338.

168. Pritchard, B. P.; Altarawy, D.; Didier, B.; Gibson, T. D.; Windus, T. L., New Basis Set Exchange: An Open, Up-to-Date Resource for the Molecular Sciences Community. *Journal of Chemical Information and Modeling* **2019**, *59* (11), 4814-4820.

169. Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A., The weighted histogram analysis method for free-energy calculations on biomolecules. I. The method. *Journal of Computational Chemistry* **1992**, *13* (8), 1011-1021.

170. Voter, A. F., Hyperdynamics: Accelerated Molecular Dynamics of Infrequent Events. *Physical Review Letters* **1997**, *78* (20), 3908-3911.



171. Laio, A.; Rodriguez-Fortea, A.; Gervasio, F. L.; Ceccarelli, M.; Parrinello, M., Assessing the Accuracy of Metadynamics. *The Journal of Physical Chemistry B* **2005**, *109* (14), 6714-6721.

172. Barducci, A.; Bonomi, M.; Parrinello, M., Metadynamics. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2011**, *1* (5), 826-843.

173. Fiorin, G.; Klein, M. L.; Hénin, J., Using collective variables to drive molecular dynamics simulations. *Molecular Physics* **2013**, *111* (22-23), 3345-3362.

174. Bal, K. M.; Neyts, E. C., Merging metadynamics into hyperdynamics: accelerated molecular simulations reaching time scales from microseconds to seconds. *J Chem Theory Comput* **2015**, *11* (10), 4545-54.

175. Awasthi, S.; Kapil, V.; Nair, N. N., Sampling free energy surfaces as slices by combining umbrella sampling and metadynamics. *J Comput Chem* **2016**, *37* (16), 1413-24.

176. Voter, A. F.; Montalenti, F.; Germann, T. C., Extending the time scale in atomistic simulation of materials. *Annual Review of Materials Research* **2002**, *32*, 321-346.

177. So; slash; rensen, M. R.; Voter, A. F., Temperature-accelerated dynamics for simulation of infrequent events. *Journal of Chemical Physics* **2000**, *112* (21), 9599.

178. Sorensen, M. R.; Voter, A. F., Temperature-accelerated dynamics for simulation of infrequent events. *Journal of Chemical Physics* **2000**, *112* (21), 9599-9606.

179. Perez, D.; Uberuaga, B. P.; Shim, Y.; Amar, J. G.; Voter, A. F., Accelerated Molecular Dynamics Methods: Introduction and Recent Developments. In *Annual Reports in*

Computational Chemistry, Vol 5, Wheeler, R. A., Ed. 2009; Vol. 5, pp 79-98.

180. Miron, R. A.; Fichthorn, K. A., Accelerated molecular dynamics with the bond-boost method. *The Journal of Chemical Physics* **2003**, *119* (12), 6210-6216.

181. Fichthorn, K. A.; Miron, R. A.; Wang, Y. S.; Tiwary, Y., Accelerated molecular dynamics simulation of thin-film growth with the bond-boost method. *Journal of Physics-Condensed Matter* **2009**, *21* (8), 9.

182. Fichthorn, K. A.; Mubin, S., Hyperdynamics made simple: Accelerated molecular dynamics with the Bond-Boost method. *Computational Materials Science* **2015**, *100*, *Part B*, 104-110.

183. Warshel, A., Dynamics of reactions in polar solvents. Semiclassical trajectory studies of electron-transfer and proton-transfer reactions. *The Journal of Physical Chemistry* **1982**, *86* (12), 2218-2224.

184. Hwang, J. K.; Warshel, A., Microscopic examination of free-energy relationships for electron transfer in polar solvents. *Journal of the American Chemical Society* **1987**, *109* (3), 715-720.

185. King, G.; Warshel, A., Investigation of the free energy functions for electron transfer reactions. *The Journal of Chemical Physics* **1990**, *93* (12), 8682-8692.

186. Kerisit, S.; Rosso, K. M., Charge transfer in FeO: A combined molecular-dynamics and ab initio study. *The Journal of Chemical Physics* **2005**, *123* (22), 224712.

187. Blumberger, J.; Sprik, M., Quantum versus classical electron transfer energy as reaction coordinate for the aqueous Ru2+/Ru3+ redox reaction. *Theoretical Chemistry Accounts* **2005**, *115* (2-3), 113-126.

188. Blumberger, J.; Sprik, M., Ab initio molecular dynamics simulation of the aqueous Ru2+/Ru3+ redox reaction: the Marcus perspective. *J Phys Chem B* **2005**, *109* (14), 6793-804.



189. Blumberger, J.; Tavernelli, I.; Klein, M. L.; Sprik, M., Diabatic free energy curves and coordination fluctuations for the aqueous Ag+Ag2+ redox couple: a biased Born-Oppenheimer molecular dynamics investigation. *J Chem Phys* **2006**, *124* (6), 64507.

190. Zhou, Z.; Long, R.; Prezhdo, O. V., Why Silicon Doping Accelerates Electron Polaron Diffusion in Hematite. *J Am Chem Soc* **2019**, *141* (51), 20222-20233.

191. Laio, A.; Parrinello, M., Escaping free-energy minima. *Proceedings of the National Academy of Sciences* **2002**, *99* (20), 12562-12566.

192. Alessandro, L.; Francesco, L. G., Metadynamics: a method to simulate rare events and reconstruct the free energy in biophysics, chemistry and material science. *Reports on Progress in Physics* **2008**, *71* (12), 126601.

193. Iannuzzi, M.; Laio, A.; Parrinello, M., Efficient exploration of reactive potential energy surfaces using Car-Parrinello molecular dynamics. *Phys Rev Lett* **2003**, *90* (23), 238302.

194. Christ, C. D.; van Gunsteren, W. F., Multiple free energies from a single simulation: extending enveloping distribution sampling to nonoverlapping phase-space distributions. *J Chem Phys* **2008**, *128* (17), 174112.

195. Marx, D.; Hutter, J., *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods*. Cambridge University Press: Cambridge, 2009.

196. Oberhofer, H.; Blumberger, J., Charge constrained density functional molecular dynamics for simulation of condensed phase electron transfer reactions. *J Chem Phys* 2009, 131 (6), 064101.

197. Ivanov, S. D.; Witt, A.; Marx, D., Theoretical spectroscopy using molecular dynamics: theory and application to CH5(+) and its isotopologues. *Phys Chem Chem Phys* **2013**, *15* (25), 10270-99.

198. van den Berg, E.; Friedlander, M. P., Probing the Pareto Frontier for Basis Pursuit Solutions. *Siam J Sci Comput* **2008**, *31* (2), 890-912.

199. Birgin, E. G.; Martinez, J. M.; Raydan, M., Spectral Projected Gradient Methods: Review and Perspectives. *J Stat Softw* **2014**, *60* (3).

200. Korbel, S.; Marques, M. A. L.; Botti, S., Stability and electronic properties of new inorganic perovskites from high-throughput ab initio calculations. *Journal of Materials Chemistry C* **2016**, *4* (15), 3157-3167.

201. Todorov, T. K.; Reuter, K. B.; Mitzi, D. B., High-efficiency solar cell with Earthabundant liquid-processed absorber. *Adv Mater* **2010**, *22* (20), E156-9.

202. Kresse, G.; Hafner, J., Ab initio molecular dynamics for liquid metals. *Phys Rev B Condens Matter* **1993**, *47* (1), 558-561.

203. Kresse, G.; Hafner, J., Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium. *Phys Rev B Condens Matter* **1994**, *49* (20), 14251-14269.

204. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 1996, *54* (16), 11169-11186.
205. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* 1996, *6* (1),

15-50.

206. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **1999**, *59* (3), 1758-1775.

207. Blochl, P. E., Projector augmented-wave method. *Phys Rev B Condens Matter* **1994**, *50* (24), 17953-17979.



208. Legrain, F.; Carrete, J.; van Roekeghem, A.; Curtarolo, S.; Mingo, N., How Chemical Composition Alone Can Predict Vibrational Free Energies and Entropies of Solids. *Chemistry of Materials* **2017**, *29* (15), 6220-6227.

209. Taylor, R. H.; Rose, F.; Toher, C.; Levy, O.; Yang, K.; Buongiorno Nardelli, M.; Curtarolo, S., A RESTful API for exchanging materials data in the AFLOWLIB.org consortium. *Computational Materials Science* **2014**, *93*, 178-192.

210. Rose, F.; Toher, C.; Gossett, E.; Oses, C.; Nardelli, M. B.; Fornari, M.; Curtarolo, S., AFLUX: The LUX materials search API for the AFLOW data repositories. *Computational Materials Science* **2017**, *137*, 362-370.

211. LaPorte, C. Modeling the Transport of Charges in Transition Metal Oxides using Small Polaron Theory Christine LaPorte. Thesis (M.S.)--State University of New York at Buffalo, 2018., 2018.

212. Liu, T. F.; Pasumarthi, V.; LaPorte, C.; Feng, Z. C.; Li, Q. Y.; Yang, J. J.; Li, C.; Dupuis, M., Bimodal hole transport in bulk BiVO4 from computation. *Journal of Materials Chemistry A* **2018**, *6* (8), 3714-3723.

213. Plata, J. J.; Márquez, A. M.; Sanz, J. F., Electron Mobility via Polaron Hopping in Bulk Ceria: A First-Principles Study. *The Journal of Physical Chemistry C* **2013**, *117* (28), 14502-14509.

214. Morbec, J. M.; Galli, G., Charge transport properties of bulkTa3N5from first principles. *Physical Review B* **2016**, *93* (3).

215. Maxisch, T.; Zhou, F.; Ceder, G., Ab initiostudy of the migration of small polarons in olivineLixFePO4and their association with lithium ions and vacancies. *Physical Review B* **2006**, *73* (10).

216. Loftager, S.; García-Lastra, J. M.; Vegge, T., A Density Functional Theory Study of the Ionic and Electronic Transport Mechanisms in LiFeBO3 Battery Electrodes. *The Journal of Physical Chemistry C* **2016**, *120* (33), 18355-18364.

217. Ding, H.; Lin, H.; Sadigh, B.; Zhou, F.; Ozoliņš, V.; Asta, M., Computational Investigation of Electron Small Polarons in α-MoO3. *The Journal of Physical Chemistry C* **2014**, *118* (29), 15565-15572.

218. Munoz Ramo, D.; Shluger, A. L.; Gavartin, J. L.; Bersuker, G., Theoretical prediction of intrinsic self-trapping of electrons and holes in monoclinic HfO2. *Phys Rev Lett* **2007**, *99* (15), 155504.

219. Hoang, K., Defect Physics, Delithiation Mechanism, and Electronic and Ionic Conduction in Layered Lithium Manganese Oxide Cathode Materials. *Physical Review Applied* **2015**, *3* (2).

220. Torrance, J. B.; Lacorro, P.; Asavaroengchai, C.; Metzger, R. M., Simple and perovskite oxides of transition-metals: Why some are metallic, while most are insulating. *Journal of Solid State Chemistry* **1991**, *90* (1), 168-172.

221. Pesaran, M. H., Time series and panel data econometrics. 2016.

222. Hastie, T.; Tibshirani, R.; Friedman, J., Boosting and Additive Trees. In *The Elements of Statistical Learning: Data Mining, Inference, and Prediction*, Springer New York: New York, NY, 2009; pp 337-387.

223. Pedregosa, F.; Varoquaux, G.; Gramfort, A.; Michel, V.; Thirion, B.; Grisel, O.; Blondel, M.; Müller, A.; Nothman, J.; Louppe, G.; Prettenhofer, P.; Weiss, R.; Dubourg, V.; Vanderplas, J.; Passos, A.; Cournapeau, D.; Brucher, M.; Perrot, M.; Duchesnay, É. Scikit-



learn: Machine Learning in Python *arXiv e-prints* [Online], 2012, p. arXiv:1201.0490. <u>https://ui.adsabs.harvard.edu/abs/2012arXiv1201.0490P</u> (accessed January 01, 2012).

224. Tripković, V.; Skúlason, E.; Siahrostami, S.; Nørskov, J. K.; Rossmeisl, J., The oxygen reduction reaction mechanism on Pt(111) from density functional theory calculations. *Electrochimica Acta* **2010**, *55* (27), 7975-7981.

225. Tritsaris, G. A.; Nørskov, J. K.; Rossmeisl, J., Trends in oxygen reduction and methanol activation on transition metal chalcogenides. *Electrochimica Acta* **2011**, *56* (27), 9783-9788. 226. Norskov, J. K.; Abild-Pedersen, F.; Studt, F.; Bligaard, T., Density functional theory in

surface chemistry and catalysis. *Proc Natl Acad Sci U S A* **2011**, *108* (3), 937-43.

227. Karp, E. M.; Campbell, C. T.; Studt, F.; Abild-Pedersen, F.; Nørskov, J. K., Energetics of Oxygen Adatoms, Hydroxyl Species and Water Dissociation on Pt(111). *The Journal of Physical Chemistry C* **2012**, *116* (49), 25772-25776.

228. Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H., Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *Journal of Physical Chemistry B* **2004**, *108* (46), 17886-17892.

229. Jahan, M.; Liu, Z. L.; Loh, K. P., A Graphene Oxide and Copper-Centered Metal Organic Framework Composite as a Tri-Functional Catalyst for HER, OER, and ORR. *Adv Funct Mater* **2013**, *23* (43), 5363-5372.

230. Shi, Y.; Wang, J.; Wang, C.; Zhai, T. T.; Bao, W. J.; Xu, J. J.; Xia, X. H.; Chen, H. Y., Hot electron of Au nanorods activates the electrocatalysis of hydrogen evolution on MoS₂ nanosheets. *J. Am. Chem. Soc* **2015**, *137* (23), 7365-7370.

231. Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F., Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials. *Acs Catal* **2014**, *4* (11), 3957-3971.

232. Zhang, H.; Hwang, S.; Wang, M.; Feng, Z.; Karakalos, S.; Luo, L.; Qiao, Z.; Xie, X.; Wang, C.; Su, D.; Shao, Y.; Wu, G., Single Atomic Iron Catalysts for Oxygen Reduction in Acidic Media: Particle Size Control and Thermal Activation. *J. Am. Chem. Soc* **2017**, *139* (40), 14143-14149.

233. Zhang, H.; Osgood, H.; Xie, X.; Shao, Y.; Wu, G., Engineering nanostructures of PGM-free oxygen-reduction catalysts using metal-organic frameworks. *Nano Energy* **2017**, *31* (Supplement C), 331-350.

234. Li, Y.; Wang, Y.; Pattengale, B.; Yin, J.; An, L.; Cheng, F.; Li, Y.; Huang, J.; Xi, P., High-index faceted CuFeS₂ nanosheets with enhanced behavior for boosting hydrogen evolution reaction. *Nanoscale* **2017**, *9* (26), 9230-9237.

235. An, L.; Li, Y.; Luo, M.; Yin, J.; Zhao, Y.-Q.; Xu, C.; Cheng, F.; Yang, Y.; Xi, P.; Guo, S., Atomic-Level Coupled Interfaces and Lattice Distortion on CuS/NiS2

Nanocrystals Boost Oxygen Catalysis for Flexible Zn-Air Batteries. *Adv Funct Mater* **2017**, 27 (42), 1703779.

236. Gao, M. R.; Jiang, J.; Yu, S. H., Solution-based synthesis and design of late transition metal chalcogenide materials for oxygen reduction reaction (ORR). *Small* 2012, 8 (1), 13-27.
237. Chia, X.; Eng, A. Y.; Ambrosi, A.; Tan, S. M.; Pumera, M., Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides. *Chem. Rev.* 2015, *115* (21), 11941-11966.

238. Zhang, Y.; Zhou, Q.; Zhu, J. X.; Yan, Q. Y.; Dou, S. X.; Sun, W. P., Nanostructured Metal Chalcogenides for Energy Storage and Electrocatalysis. *Adv Funct Mater* **2017**, *27* (35), 1702317.



239. Cho, K.; Han, S. H.; Suh, M. P., Copper-Organic Framework Fabricated with CuS Nanoparticles: Synthesis, Electrical Conductivity, and Electrocatalytic Activities for Oxygen Reduction Reaction. *Angew. Chem. Int. Ed. Engl.* **2016**, *55* (49), 15301-15305.

240. Wang, X.; Ke, Y.; Pan, H.; Ma, K.; Xiao, Q.; Yin, D.; Wu, G.; Swihart, M. T., Cu-Deficient Plasmonic Cu2–xS Nanoplate Electrocatalysts for Oxygen Reduction. *Acs Catal* **2015**, *5* (4), 2534-2540.

241. Kim, C. S.; Choi, S. H.; Bang, J. H., New insight into copper sulfide electrocatalysts for quantum dot-sensitized solar cells: composition-dependent electrocatalytic activity and stability. *ACS Appl. Mater. Interfaces* **2014**, *6* (24), 22078-87.

242. An, L.; Zhou, P.; Yin, J.; Liu, H.; Chen, F.; Liu, H.; Du, Y.; Xi, P., Phase transformation fabrication of a Cu₂S nanoplate as an efficient catalyst for water oxidation with glycine. *Inorg. Chem.* **2015**, *54* (7), 3281-3289.

243. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys Rev Lett* **1996**, *77* (18), 3865-3868.

244. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

245. Kresse, G.; Hafner, J., Ab-Initio Molecular-Dynamics for Open-Shell Transition-Metals. *Phys. Rev. B* **1993**, *48* (17), 13115-13118.

246. Kresse, G.; Hafner, J., Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, *49* (20), 14251-14269.

247. Kresse, G.; Furthmuller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, *54* (16), 11169-11186.
248. Blöchl, P. E., Projector augmented-wave method. *Phys. Rev. B* 1994, *50* (24), 17953-17979.

249. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59* (3), 1758-1775.

250. Wisesa, P.; McGill, K. A.; Mueller, T., Efficient generation of generalized Monkhorst-Pack grids through the use of informatics. *Phys. Rev. B* **2016**, *93* (15), 155109.

251. Valdés, Á.; Qu, Z. W.; Kroes, G. J.; Rossmeisl, J.; Nørskov, J. K., Oxidation and Photo-Oxidation of Water on TiO2 Surface. *J Mater Chem C* **2008**, *112* (26), 9872-9879.

252. Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H., Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108* (46), 17886-17892.

253. Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A., Electric-field induced intramolecular electron transfer in spiro .pi.-electron systems and their suitability as molecular electronic devices. A theoretical study. *Journal of the American Chemical Society* **1990**, *112* (11), 4206-4214.

254. Mathew, K.; Montoya, J. H.; Faghaninia, A.; Dwarakanath, S.; Aykol, M.; Tang, H.; Chu, I.-h.; Smidt, T.; Bocklund, B.; Horton, M.; Dagdelen, J.; Wood, B.; Liu, Z.-K.; Neaton, J.; Ong, S. P.; Persson, K.; Jain, A., Atomate: A high-level interface to generate, execute, and analyze computational materials science workflows. *Computational Materials Science* **2017**, *139*, 140-152.

255. Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G., Python Materials Genomics (pymatgen): A robust,



open-source python library for materials analysis. *Computational Materials Science* **2013**, *68*, 314-319.

