Ab Initio Simulations in Materials Science

Hands-On Introduction to Electronic Structure Modeling with VASP

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Table of Contents

1. Preface

First-principles (ab initio) simulations are indispensable in materials science due to their ability to provide fundamental insights into the behavior and properties of materials at the atomic and electronic levels. Unlike empirical or semi-empirical methods, first-principles simulations are based solely on fundamental physical principles, such as quantum mechanics, without requiring experimental data as input. This enables researchers to predict the properties of materials with unprecedented accuracy and understand their behavior under various conditions, aiding in the design of novel materials with tailored functionalities. Moreover, these simulations allow for the exploration of materials under extreme conditions that are difficult or impossible to achieve experimentally, providing invaluable insights into phenomena such as high-pressure behavior, chemical reactions, and electronic transport at nanoscales. By elucidating the underlying mechanisms governing material behavior, first-principles simulations play a crucial role in advancing our understanding of complex materials systems and accelerating the development of innovative technologies across numerous fields, including energy storage, catalysis, electronics, and nanotechnology.

First-principles methods and empirical methods represent two distinct approaches in theoretical chemistry and computational materials science, each with its own set of advantages and limitations. First-principles methods, such as density functional theory (DFT) and ab initio quantum chemistry methods, rely on solving the fundamental equations of quantum mechanics to calculate electronic structure and molecular properties from basic principles, without the need for experimental data or empirical parameters. These methods offer high accuracy and are particularly valuable for studying small to medium-sized molecules and systems where precise quantum mechanical calculations are essential. On the other hand, empirical methods, including molecular mechanics and force field approaches, approximate the potential energy surface of a molecule based on empirical parameters derived from experimental data or quantum calculations. While empirical methods are computationally less demanding and suitable for studying larger molecular systems and biomolecules, they sacrifice accuracy for computational efficiency and rely heavily on parameterization, which can limit their applicability to systems that significantly deviate from the training set. Thus, the choice between first-principles and empirical methods in computational chemistry often depends on the specific research objectives, the size and complexity of the system under investigation, and the balance between accuracy and computational cost.

Classical mechanics and quantum mechanics are two fundamental theories that describe the behavior of physical systems at different scales. Classical mechanics, developed by Newton and later refined by Euler, Lagrange, and Hamilton, provides a framework for understanding the motion of macroscopic objects based on Newton's laws of motion and the principle of conservation of energy and momentum. It successfully describes the behavior of objects at everyday scales, such as planets orbiting the Sun or balls moving on a billiard table, using deterministic equations of motion. In contrast, quantum mechanics, formulated by pioneers like Bohr, Planck, Heisenberg, Schrödinger, and Dirac, describes the behavior of particles at the atomic and subatomic levels. Quantum mechanics introduces probabilistic behavior and wave-particle duality, challenging the intuitive notions of classical physics. It provides a statistical framework for understanding phenomena like particle-wave interference, the quantization of energy levels, and the uncertainty principle. While classical mechanics provides an excellent approximation for large-scale systems, quantum mechanics is indispensable for describing the behavior of particles at microscopic scales and is the foundation of modern physics and chemistry. Despite their differences, both theories are essential pillars of physics, each applicable in its respective domain of validity.

The primary aim of this book is to equip readers with the fundamentals in Quantum Mechanics, essential for comprehending first-principles simulations. Unlike Classical Mechanics, governed by Newtonian laws yielding predictable trajectories, Quantum Mechanics operates on the probabilistic distribution of permissible quantum states. While our intuition naturally grasps Classical Mechanics laws due to our evolution in that realm, comprehending Quantum Mechanics proves challenging due to the absence of clear motion trajectories and the probabilistic nature inherent in atomic and subatomic physics. Hence, we embark on this journey by elucidating three fundamental motions in the atomic domain: the particle in a potential box, quantum oscillator, and quantum rotator. These three cornerstone motions bridge the gap between classical mechanics in the macroscopic world and quantum mechanics in the atomic and subatomic realms. With a grasp of these motions, we can tackle the simplest chemical problem: the hydrogen atom. Notably, we will uncover how the electron's behavior within the proton's potential field intimately relates to core quantum mechanical problems like the particle in a potential box, quantum oscillator, and quantum rotator.

We will draw a direct connection between the quantum oscillator problem and the formation of chemical bonds, establishing the groundwork for vibrational infrared spectroscopy. Transitioning from the one-electron Schrödinger equation for the hydrogen atom, we will extend our exploration to the many-electron Schrödinger equation, illuminating a fundamental physical barrier that obstructs direct analytic first-principles solutions for many-electron systems. Tracing the historical trajectory, we will explore a series of approximations developed to address the challenge of many-electron systems numerically. These approximations culminate in the Hartree-Fock (HF) method, marking a significant milestone in quantum mechanical approaches capable of addressing real-world problems in chemistry and materials science. However, we will also uncover the limitations of the Hartree-Fock approach, confining its applicability to a select number of molecules and materials. Before delving into density functional theory, we will briefly survey post-Hartree-Fock methods, looking at deeper exploration of computational chemistry methodologies.

Our exploration of density functional theory commences with an examination of the Hohenberg-Kohn theorem and the Kohn-Sham equations, which stand as the cornerstone of Walter Kohn's Nobel Prize-winning work in 1996. Delving deeper, we will look at the methodology of the Local Density Approximation (LDA) and the pioneering Perdew-Zunger (PZ) functional before transitioning to the widely embraced Generalized Gradient Approximation (GGA) and the contemporary metaGGA and hybrid functionals. Through this journey, we aim to unravel these theoretical frameworks, shedding light on their evolution and significance in advancing our understanding of quantum mechanics in chemistry and materials science.

We will explore the Bloch theorem for periodic boundary conditions and investigate its practical implications concerning the comprehension of reciprocal space and the selection of K-points in numerous DFT codes. This inquiry extends to uncovering the underlying principles of band structures, interpreting density of states plots, and understanding their connection to bond strengths, electron localization/delocalization phenomena, and conductivity. Furthermore, we will examine the construction of wavefunctions using atomic basis sets, such as the Linear Combination of Atomic Orbitals (LCAO) method. Our discussion will also include a concise overview of the systematic Pople basis set construction, which plays a fundamental role in the Gaussian program. Subsequently, our attention will turn towards the planewave wavefunction and the pseudopotential method, exploring how accuracy is controlled through parameters like planewave cutoff energies and pseudopotential hardness.

Once we conclude our exploration of electronic simulations, our focus will shift to nuclei motion. This phase involves a thorough examination of the Born-Oppenheimer approximation and the separation between nuclei and electronic degrees of freedom. We will compare classical and quantum Hamiltonians before delving into the derivation of Hellmann-Feynman electrostatic forces. Exploring optimization strategies, we will look at popular algorithms such as conjugated gradient and quasi-Newton optimizers. Additionally, we will touch upon advanced optimizers available through external packages like the Vasp Transition State Tool by the Henkelman group. We will move to first-principles molecular dynamics and will cover different ensembles and the theoretical fundamentals. This exploration will lead us to discussions on Transition State Theory and the implementation of the Nudged Elastic Band (NEB) method. Concluding the theoretical segment, we will provide an overview of the DFT+U method for highly correlated systems, an overview of the Non-Equilibrium Green’s Function method along with a comparative discussion on available DFT software, weighing their advantages and disadvantages.

The theoretical portion is accompanied by practical guidance and real-world examples showcasing the application of VASP software in materials science. While not an exhaustive VASP tutorial, this book draws from the author's two decades of experience in scientific research utilizing VASP, with insights distilled from over 100 peer-reviewed publications. It is important to note that the author has no affiliation with the VASP developer team. Rather, this book aims to share valuable insights, guiding readers through common hurdles and providing efficient solutions. By emphasizing best practices for reliable and reproducible results, it serves as a knowledge repository, offering beginners a swift introduction and practical tips to tackle scientific tasks effectively in real-world scenarios. Our practical guide begins with an installation tutorial tailored for Ubuntu systems. Although VASP can be compiled on various platforms, such as different Linux distributions, UNIX machines, graphic cards, and even MacOS, the compilation process often requires expertise in settings and a deep understanding of compilers and processor architectures. However, many novice materials scientists aim to swiftly set up their computational systems and dive into computational materials science. Hence, this book focuses on installing the parallel version of VASP on a multicore Ubuntu box, given its widespread use and user-friendly interface among Linux operating systems. Additionally, we will provide a tutorial on compiling VASP for the novel (as of 2024) Apple Silicon chips, known for their remarkable productivity and ease of use.

The compilation instruction will be followed by the four essential VASP files: POSCAR (and CONTCAR), INCAR, POTCAR, and KPOINT. Those files are the minimum requirement for a user to execute VASP and perform simulations with it. We will look at the electronic self consistent loop and the control parameter which affect its accuracy and efficiency which will be followed by a chapter on geometry optimization with detailed description on optimization routines for cell and atomic relaxation and various optimizers. The electronic structure calculations will be followed by density of states (DOS) analysis and plot routines and band structure calculations. We will see how the density of states can be split into orbitals and atoms, i.e., partial DOS or pDOS. Transition state theory will be covered by the nudged elastic band method and the Vasp Transition States Tools. We will look into the computational routine for diffusion coefficients in solids including preexponential factor. The VTST extension of VASP contains various force-based optimizers which are missing in the original VASP distribution. The differences of the optimizers will be discussed, and the efficiency control parameters will be highlighted.

Accurate electronic correlation is missing in the common GGA functional which is a significant problem when we study highly-correlated systems such as complex oxides. The problem affects band gaps, electronic spectra, activation barriers for chemical reactions, and diffusion coefficients. An efficient method to include the correlation energy trough (empirical) parameter is the DFT+U method. It is implemented in VASP and allows various control options. The U and J parameters can be applied to different electronic shells and elements. Another way to approach the electron correlations in VASP is the use of hybrid and metaGGA functionals. We will discuss the theory and implementation of the widely used functionals such a HSE06 and PBE0. The convergence of hybrid functionals requires additional settings and self consistent runs. The newly implemented metaGGA functionals allow us to use a complete first-principles treatment avoiding any empirical parameters. We will revise functionals used for accurate reaction energetics and also functionals capable to reproduce accurately the band gaps and electronic properties. We will look into various convergence problems and deal with workflows to accelerate the calculations.

First principle molecular dynamics will be introduced for study of ensembles of molecules, ionic diffusion, and surface adsorption. We will discuss the settings and parameters such as time step, thermostats, and data analysis. We will look at the important technique: computational annealing which is a useful preoptimization routine. Vibrational calculations in VASP and their application for attempt frequency calculations on pre exponential factor will be explained. The book contains various python codes in the Appendix for acerated simulations and representation of atomistic data.

About the author

Dr. Aleksandar Staykov earned his Master of Science degree in Organic Chemistry from Sofia University, Bulgaria, in 2002, under the supervision of Prof. Nikolai Tyutyulkov. He then pursued doctoral studies at the Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, Leipzig University, Germany, where he was awarded his Ph.D. (Dr. rer. nat.) *magna cum laude* in 2006. His doctoral dissertation, titled *"Magnetic and Electronic Properties of One-Dimensional Stacks of Polycyclic Aromatic Hydrocarbons"*, was supported by a fellowship from the German Academic Exchange Service (DAAD), with supervision by Prof. Fritz Dietz and Prof. Nikolai Tyutyulkov.

Since 2006, Dr. Staykov has been affiliated with Kyushu University, Japan. He began as a postdoctoral fellow under the Japan Society for the Promotion of Science (JSPS), working with Prof. Kazunari Yoshizawa at the Institute for Materials Chemistry and Engineering. In 2011, he joined the International Institute for Carbon-Neutral Energy Research (WPI-I^{2}CNER), where he currently serves as a tenured Associate Professor in the Department of Applied Chemistry and as a Principal Investigator at I^{2}CNER.

Dr. Staykov teaches the courses *Thermodynamics* and *Design of Quantum Materials*. His laboratory specializes in theoretical and computational chemistry, employing first-principles calculations to investigate the properties of solids, surfaces, and interfaces. His research utilizes advanced techniques such as density functional theory (DFT), the non-equilibrium Green's function method, and first-principles molecular dynamics.

His work is dedicated to the simulation of materials for renewable energy technologies. This includes the study of chemical processes at the surfaces and interfaces of complex oxides used in solid oxide fuel cells, the behavior of nanoparticles and nanostructures in catalysis, and the electronic properties of junctions and interfaces relevant to nanoelectronics and solar energy applications.