

Computational Mineral Physics

Computational mineralogy is fast becoming the most effective and quantitatively accurate method for successfully determining structures, properties, and processes at the extreme pressure and temperature conditions that exist within the Earth's deep interior. It is now possible to simulate complex mineral phases using a variety of theoretical computational techniques that probe the microscopic nature of matter at both the atomic and subatomic levels. This introductory guide is for geoscientists and researchers performing measurements and experiments in a lab, those seeking to identify minerals remotely or in the field, and those seeking specific numerical values of particular physical properties. Written in a user- and property-oriented way and illustrated with calculation examples for different mineral properties, it explains how property values are produced, how to tell if they are meaningful or not, and how they can be used alongside experimental results to unlock the secrets of the Earth.

Razvan Caracas is a computational mineral physicist with a background in both geology and materials sciences. He was awarded a PhD from the Catholic University of Louvain prior to holding a postdoctoral position at the University of Minnesota, a Carnegie Fellowship at the Carnegie Institution of Washington, and a Humboldt Fellowship at the University of Bayreuth. He is a Fellow of the Mineralogical Society of America, a recipient of the Dana Medal of the same society, and a member of the Academia Europaea. He was a CNRS researcher at the Ecole Normale Supérieure de Lyon, and adjunct professor at the Center for Planetary Habitability of the University of Oslo. He is presently a senior researcher at the Institute de Physique du Globe de Paris, working on a wide range of topics in planetary mineralogy, going from the supercritical state that dominated the protolunar disk to the internal structure of exoplanets. With the help of atomistic simulations, his work explores the early Earth's evolution – helping to decipher the condensation of the Earth and the Moon, the formation of the primordial atmosphere, and exploring what conditions planets must fulfil to make prebiotic chemistry thrive.

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A Practical Guide for Earth Scientists

RAZVAN CARACAS

Institut de Physique du Globe de Paris, CNRS, Université Paris Cité



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In memory of my father.

Contents

<i>List of Boxes</i>	page xi
<i>Preface</i>	xiii

Part I Getting Started

1	Introduction	3
1.1	The Internal Structure of the Earth	3
1.2	A Few Words about Thermodynamics	7
1.3	Notions of Crystallography. Symmetry, and the Direct Space	12
1.4	The Reciprocal Space	21
1.5	Tensors	22
1.6	A Few Unix/Linux Commands	25
1.7	Some Special Notations in Quantum Mechanics	27
2	Atomistic Calculations Using Interatomic Potentials	29
2.1	General Considerations about Potentials	29
2.2	Pair-Wise Interatomic Potentials	30
2.3	Multi-Body Potentials	32
2.4	Interatomic Potentials for Metals	35
2.5	Force Fields	36
2.6	Requirements for Good Interatomic Potentials	38

Part II Static Properties

3	Density Functional Theory	43
3.1	Kohn–Sham Equations	45
3.2	Exchange–Correlation	47
3.3	Planewaves and k-Points	50
3.4	Pseudopotentials	56
3.5	Beyond Standard Pseudopotential-Based DFT	61
3.6	Projector Augmented-Wave (PAW) Method	62
3.7	Quantum Monte Carlo	64
4	Static Electronic Properties	68
4.1	Internal Electronic Energy	68
4.2	Electronic Density	69
4.3	Static Atomic Charges	71
4.4	Brillouin Zone	75

4.5	Electronic Band Structure	78
4.6	Metals versus Insulators	90
4.7	A Few More Examples and Interpretations of the Electronic Band Structure for Minerals	97
5	Origin of Colour, Optical Constants, and Electronic Spectroscopy	106
5.1	Interaction of Light with Metals and Insulators	106
5.2	Crystal Field Theory	107
5.3	Electronic Spectroscopies	109
5.4	Optical Constants and the Problem of the Electronic Gap	111
5.5	Hubbard U and J Parameters	112
5.6	Beyond and Alternatives to DFT+U	114
6	Magnetism	115
6.1	Magnetic Hysteresis	117
6.2	Curie and Néel Temperature and the Origin of Palaeomagnetism	119
6.3	Contributions of DFT Calculations	120
7	Polarisation	123
7.1	The Berry Phase and the Value of Polarisation	124
7.2	Ferroelectricity	126
7.3	Piezoelectricity and Piezomagnetism	128
7.4	Multiferroics	129
8	Mechanical Properties	131
8.1	The Stress Tensor and the Pressure	131
8.2	Structural Relaxations	133
8.3	Compressibility and the Equation of State	138
8.4	Static Transition Pressure	142
8.5	Hardness	145
8.6	Elastic and Compliance Tensors	145
8.7	Seismic Wave Velocities	147
8.8	Rheology and Deformation	153
Part III Dynamical Properties		
9	Lattice Dynamics	159
9.1	Potential Energy Wells	159
9.2	Taylor Expansion of the Energy	163
9.3	Quasiharmonic Approximation	165
9.4	Coupled Perturbations	167
9.5	Energy Derivatives as Physical Observables	168
10	Density-Functional Perturbation Theory	170
10.1	Energy Derivatives from Finite Differences	170
10.2	Energy Derivatives from Perturbation Theory	170

11 Dielectric Properties	174
11.1 Polarisation as Energy Derivative	174
11.2 Born Effective Charges	175
11.3 Dielectric Tensor and Refractive Index	179
11.4 Non-linear Optical Properties	181
12 Phonons	183
12.1 Interatomic Force Constants	183
12.2 The Dynamical Matrix	187
12.3 Eigenvectors of the Dynamical Matrix	190
12.4 Eigenvalues of the Dynamical Matrix	191
12.5 Vibrational Patterns	192
12.6 The Γ Point	196
12.7 Irreducible Representations (<i>irreps</i>)	198
12.8 Phonon Dispersion	201
12.9 Phonon Density of States	205
12.10 Instabilities	205
13 Vibrational Spectroscopy	208
13.1 Infrared Spectroscopy	208
13.2 Raman Spectroscopy	211
13.3 Brillouin Spectroscopy	219
14 A Few Examples of Phonon Analysis	222
14.1 Halite, NaCl	222
14.2 Sphalerite, ZnS	225
14.3 Zincite, ZnO, and Wurtzite, ZnS	228
14.4 Jadeite, NaAlSi ₂ O ₆	228
14.5 Pyrite, FeS ₂	231
14.6 Lower-Mantle Perovskites: CaSiO ₃ and Bridgmanite, MgSiO ₃	232
15 Advanced Topics in Density Functional Perturbation Theory	238
15.1 Thermodynamics	238
15.2 Strain Perturbations and a Modern View of the Elastic Constants	241
15.3 Mass-Dependent Isotope Fractionation	245
15.4 Anharmonicities: Beyond the Quasi-Harmonic Approximation	251
16 Molecular Dynamics	254
16.1 The Essentials of Molecular Dynamics	254
16.2 Atomic Displacements	255
16.3 Trajectories	259
16.4 The Simulation Box	260
16.5 Ergodicity	262
16.6 Ensembles and Averaged Properties	263

16.7	Thermostats and Barostats	264
16.8	Other Practical Aspects of the Machinery Behind Molecular Dynamics Simulations	267
17	Analysis of the Molecular Dynamics Simulations	276
17.1	General Considerations	276
17.2	Pair Distribution Function	276
17.3	Chemical Speciation	281
17.4	Atomic Diffusion in a Fluid	283
17.5	Vibrational Spectra	286
17.6	Viscosity of a Fluid	291
18	Computational Perspectives	294
	<i>References</i>	296
	<i>Index</i>	311

Boxes

1.1	What is a crystal structure?	<i>page</i> 19
3.1	What is a low-dimensional solid?	48
3.2	How to choose the exchange–correlation formalism?	49
3.3	How to choose the grid of k points?	53
3.4	What happens during a DFT calculation?	54
3.5	How to check convergence with respect to planewaves?	56
3.6	How to check convergence with respect to k points?	58
4.1	How to calculate the energy of quartz?	69
4.2	How to calculate the heat of formation from elements?	70
4.3	How to calculate the electronic density?	71
4.4	How to compute the Bader atomic charges?	72
4.5	How to calculate the electronic band structure?	82
4.6	How to calculate the electronic density of states?	87
4.7	How to automatise the electronic DOS calculation in solid solutions?	89
4.8	How to calculate the partial electronic density of states?	90
5.1	How to do an LDA + U calculation?	113
6.1	How to perform a collinear spin-polarised magnetic calculation?	120
6.2	How to perform a non-collinear spin-polarised magnetic calculation?	121
7.1	How to compute the spontaneous polarisation using the Berry phase?	125
8.1	How to perform a structural relaxation?	135
8.2	How to calculate the equation of state?	140
8.3	How to calculate the transition pressure?	143
8.4	How to calculate the B1–B2 transition pressure for NaCl?	143
8.5	How to calculate the elastic constants tensor?	149
8.6	How to calculate the orthorhombic elastic constants?	150
8.7	How to calculate the γ surface?	155
9.1	How to determine the potential well?	162
11.1	How to compute the Born effective charges?	180
11.2	How to compute the dielectric tensors?	182
12.1	How to build the interatomic force constants matrix?	186
12.2	How to extract the interatomic force constants?	188
12.3	How to handle the files with the energy derivatives?	189
12.4	How to compute the phonons in Γ ?	199
12.5	How to determine the irreps?	201
12.6	How to calculate the phonon dispersion?	202

12.7	How to calculate the phonon density of states?	206
13.1	How to compute the infrared reflectivity spectrum?	210
13.2	How to prepare the computation of the Raman spectrum?	214
13.3	How to calculate the Raman spectrum?	215
14.1	How to calculate the phonon dispersion of sphalerite, ZnS?	227
15.1	How to calculate the thermodynamic parameters?	240
15.2	How to calculate the elastic constants matrix?	244
16.1	How to set up the simulation box for molecular dynamics?	261
16.2	How to set up the mass of the thermostat?	267
17.1	How to choose between different diffusion analyses?	286

Preface

If you would have the courage to walk in a session on theoretical mineralogy at one of the big conferences in earth sciences (American Geophysical Union Conference, European Geosciences Union Conference, Goldschmidt, etc.), you would probably be *rained down* with the following abbreviations: DFT, PAW, GGA, PBE, XC, WC90, B3LYP, +U, and so on. Unless you were an expert active in the field for years or a highly achieving student familiar with all this foreign language, you would be lost and stop paying attention pretty soon. Alas, you would probably lose an entirely beautiful piece of science, or you wouldn't be able to say if it's the correct choice or not, if LDA is *good enough*, or if one would need GGA or meta-GGA, or if highly accurate, but computationally expensive QMC is really worth the effort.

This book tells the story of what happens during the long hours a simulation runs on a (super)computer. It tries to teach you how to perform such a simulation. Which number is important, why and how much, and what are all those abbreviations? It tries to show you what you could learn from that simulation and how to judge the quality of that particular theoretical result.

The large majority of the examples in this book are realized using the abinit package (<https://www.abinit.org/>).

This book is for geoscientists in the broadest possible sense: those who want to have a first guide into performing first-principles calculations, those who do measurements and experiments in a lab, those who try to identify minerals remotely or in the field, and those who need specific numerical values of some physical properties. Advanced master students, PhD students, and postdoctoral and young researchers who want to explore the numerical world of mineralogy will have a first taste in the pages of this book. Confirmed researchers in complementary fields, like experimental mineralogy and petrology, geochemistry, or geodynamics, will find explanations and seek understanding for the origin and meaningfulness of particular numerical results provided by their theoretician colleagues. The book spares the reader the unnecessary theoretical details and lengthy equations and instead focuses on the practical aspects of producing and interpreting useful numbers, particularly in mineralogy.

In-depth reviews of various sorts have been written about almost every imaginable technique and aspect of earth sciences, except for atomistic computational mineralogy. This book tries to fill this gap in the geoscience literature today.

Chapter 1 introduces the reader to the basis of crystallography necessary to set up the atomic arrangements for the input files of the simulations. Chapter 2 briefly discusses the topic of phenomenological interatomic potentials, their use in large-scale simulations, and also their limitations. Chapters 3, 9, 10, and 16 form the theoretical core of the entire computational mineral physics. Chapter 3 presents the foundations of the density functional theory and describes the numerical implementations and the common approximations employed. Computations of electronic properties are covered in Chapters 4 and 5, ferroic properties in Chapters 6 and 7, and mechanical properties in Chapter 8. Chapter 9 introduces the dynamical properties, the treatment of small perturbations in terms of the development of energy as Taylor series, and the quasi-harmonic approximation. Their actual computation, in the framework of the perturbation theory, is explained in Chapter 10. The calculations of various dynamical properties are discussed in Chapters 11–15. Chapter 15 is of particular interest to geochemists, who will find here the foundations of isotope fractionation. This is followed by illustrative examples of simulations of melts and fluids in Chapters 16 and 17. The book ends with a few words about supercomputers and large-scale simulations.

At the end of reading the book, the interested reader should hopefully be able to perform first-principles calculations on their own. But the main purpose is to cover as much as possible practical aspects, rather than pure theory. The entire computational machinery will be put into motion, and the steps of how to compute specific physical properties and how to judge the quality of the results will be thoroughly discussed. Reading the book should come after advanced classes in solid-state and statistical physics, typically from a strong master's or doctoral curriculum.

And a final, personal note. My voyage to computational mineral physics was meandrous, with many bricks accumulating over time. Oscillating between physics and biology, computer science and geology, this path was marked by many people's presence and knowledge. After a short physics and computational period, geology offered me a much-needed window into the natural world. From the beginning of my geology years, a unique role in my career and life played Prof. Gyuri Ilinca, who made me discover the beauty of crystallography and mineralogy and whose correspondence was highly inspiring in many ways. Then the geology professors at the University of Bucharest, Romania, like Professors Nicolae Anastasiu, Gheorghe C. Popescu, Marin Seclaman, Emil Constantinescu, and others, the colleagues, and the assistant professors chiselled my geological view of the world. After my geology years, Professor Xavier Gonze, in the ABINIT group at Louvain-la-Neuve, Belgium, saved me from the entropy of the university and accepted me in his group, where he made me fully appreciate my return to computational materials science; I am highly grateful to him for all those years. During this time, Professor Philippe Sonnet's understanding smoothed my transition from crystallography and descriptive mineralogy to physics. Later on, in the cold winter

of Minnesota, Professor Renata Wentzcovitch introduced me to the fascinating world of the deep Earth, and I thank her sincerely for this. The following years in the Geophysical Laboratory at the Carnegie Institution of Washington, USA, where I learnt so much from the staff scientists, and especially Drs Ron Cohen and Russ Hemley, completed my association with the extreme conditions. Many pages of this book were written in Oslo, and I warmly thank Carmen Gaina, Trond Torsvik, Stephanie Werner, and the entire Earth Evolution and Dynamics (CEED)/Center for Planetary HABitability (PHAB) team for hosting me so many times and offering many insightful discussions about earth sciences. Special thanks go to Chris Mohn, Mandy Bethkenhagen, Tim Bögels, and Wendy Panero for reading many parts of this manuscript and providing valuable insight. I would also like to thank the staff of the supercomputing centres in France, such as Centre Informatique National de l'Enseignement Supérieur (CINES), Centre de calcul pour la recherche et la technologie (CCRT), and the Institut du développement et des ressources en informatique scientifique (IDRIS), for their longstanding computational and technical support, as well as the Laboratory of Geology of Lyon, the Centre Blaise Pascal, and the PSMN supercomputing centre of the Ecole Normale Supérieure de Lyon, France, for their continuous support and for hosting me and my group. Over the years, countless interactions and immeasurable advice from so many other colleagues and friends, younger and older, as well as students and professors, whose names are too many to list here, helped me gain a physical and materials-oriented understanding of the natural world, which you might retrieve as well in this book. Last but not least, I deeply thank my parents, Gabriela and Virgiliu, my daughter Sarah, and my partner Cécile, for their support that long precedes and outlasts the writing of this book.