国家出版基金项目
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From Electronic Structures to Molecular Dynamics

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李新征　王恩哥　著

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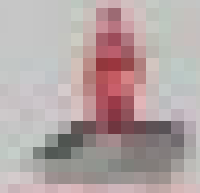
PEKING UNIVERSITY PRESS



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图书在版编目(CIP)数据

分子及凝聚态系统物性的计算模拟:从电子结构到分子动力学 = Computer simulations of molecules and condensed matters: from electronic structures to molecular dynamics / 李新征, 王恩哥著. —北京:北京大学出版社, 2014.12
(中外物理学精品书系)
ISBN 978-7-301-25152-2

Ⅰ. ①分… Ⅱ. ①李…②王… Ⅲ. ①电子结构—计算—模拟②分子动力—计算—模拟③凝聚态—物理学—计算—模拟 Ⅳ. ①O552.5②O561③O469
中国版本图书馆 CIP 数据核字(2014)第 273376 号

书　　名: **Computer Simulations of Molecules and Condensed Matters: From Electronic Structures to Molecular Dynamics(分子及凝聚态系统物性的计算模拟:从电子结构到分子动力学)**
著作责任者: 李新征　王恩哥　著
责 任 编 辑: 尹照原
标 准 书 号: ISBN 978-7-301-25152-2/O · 1035
出 版 发 行: 北京大学出版社
地　　址: 北京市海淀区成府路 205 号　100871
网　　址: http://www.pup.cn
新 浪 微 博: @北京大学出版社
电 子 信 箱: zpup@pup.pku.edu.cn
电　　话: 邮购部 62752015　发行部 62750672　编辑部 62752021
出版部 62754962
印　刷　者: 北京中科印刷有限公司
经　销　者: 新华书店
730 毫米 ×980 毫米　16 开本　18 印张　314 千字
2014 年 12 月第 1 版　2014 年 12 月第 1 次印刷
定　　价: 88.00 元

序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，“中外物理学精品书系”力图完整呈现近现代世界和中国物理科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会　主任
中国科学院院士，北京大学教授
王恩哥
2010 年 5 月于燕园

Preface

State-of-the-art computer simulation of molecules and condensed matters, according to the Born-Oppenheimer approximation, requires an accurate *ab initio* treatment of both the electronic structures and the nuclei's motion on (and sometimes even beyond) the corresponding potential energy surfaces. As a student majoring in computational condensed matter physics, one of the authors (Xin-Zheng Li, XZL) had taken many years to understand this simple sentence. During this time, his work in collaboration with Prof. Jianbai Xia and Prof. Enge Wang as well as other scholars in Europe (Prof. Angelos Michaelides, Prof. Dr. Matthias Scheffer, Dr. Ricardo Gómez-Abal, and Prof. Dr. Claudia Draxl, etc.) has luckily spanned some topics in both regimes. Based on this limited, yet to a certain extend unique, experience, the authors want to share with the readers, especially those Chinese graduate students majoring in computational condensed matter physics or chemistry, their understanding of this rapidly growing field. Special focus will be put on the basic principles underlying the present electronic structure calculations and the molecular dynamics simulations. A wide range of electronic structure theories will be introduced, including traditional quantum chemistry method, density-functional theory, many-body perturbation theory etc.. Besides these electronic structures, motions of the nuclei will also be described using molecular dynamics, with extensions to enhanced sampling and free-energy calculation techniques including umbrella sampling, meta-dynamics, integrated tempering sampling, etc., and the thermodynamic integration methods. As a further extension beyond the standard Born-Oppenheimer molecular dynamics, some simulation techniques for descriptions of the quantum nuclear effects will also be discussed, based on Feynman's path-integral representation of the quantum mechanics. With such a choice of theories on both the electronic structures and molecular dynamics perspectives, hopefully, we can help those graduate students to find the proper recipe in tackling the physical/chemical problems they are interested in.

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Introduction to Computer Simulations of Molecules and Condensed Matter

Since the discovery of electron as a particle in 1896-1897, the theory of electrons in matter has ranked among the great challenges in theoretical physics. The fundamental basis for understanding materials and phenomena ultimately rests upon understanding electronic structure. [1]

It is without any hesitation that we assent to R. M. Martin's point of view and take it as the first sentence when it comes to writing the introduction of this book on computer simulations of molecules and condensed matters. The electrons, being an interacting many-body entity, behave as a quantum glue which holds most of the matters together. Therefore, principles underlying the behavior of these electrons determine to a large extent properties of the system (electronic, optical, magnetic, mechanical, etc.) we are going to investigate. As a consequence, introduction to the computer simulation of molecules and condensed matters should naturally start from theories of electronic structures.

One point implied in this statement is that the concept of electronic structures is polymorphous, in the sense that it covers all properties related to the electrons in matter. For example, it can refer to the total energy of the electrons, their density distribution, the energy needed for extracting (injecting) one electron out of (into) the system, their response to an external perturbation, etc.. These properties are in principle measured by different experiments and described using different theoretical methods. Therefore, when saying "electronic structures", one must specify the specific property of the electrons it refers to and the theory we are using. Among the various properties and theories in describing the electronic system, we will focus on the ones concerning depicting the total energies and the spectroscopies of the system within the *ab initio* framework throughout this book. For electronic

structure theories based on model Hamiltonian, e.g. the effective-mass envelope function and the tight-binding methods, which are equally important in molecular simulations but will not be discussed here, please refer to the seminal book of R. M. Martin in Ref. [1].

Besides the behavior of the electrons, the motion of the nuclei is another aspect one must accurately address in simulating the material properties, since a real material is composed by interacting electrons and nuclei. To describe such a correlated motion, some basic concepts underlying our daily research must be introduced, among which the Born-Oppenheimer approximation and the potential energy surface are the most crucial. Because of this, in the following we start our discussions by introducing these two concepts. Using these concepts, we can categorize the majority of the tasks we want to fulfill in daily researches concerning simulations of material properties into two different regimes, *i.e.* those concerning mainly the electronic structures and those concerning mainly the nuclear motion. The whole book is then organized according to such a categorization. In Chap. 2–4, we discuss different electronic structure theories and some technical details concerning their implementation. After that, Chap. 5–7 focus on the molecular dynamics (MD) method and its various extensions in descriptions of the nuclear motion. With this choice of theories on both the electronic structures and the molecular dynamics levels, we hope that we can help those graduate students to find the proper recipe in tackling the physical/chemical problems they are interested in their practical researches.

1.1 Born-Oppenheimer Approximation and the Born-Oppenheimer Potential Energy Surface

Before we start, let us first present the key equation we are going to tackle in simulating properties of a real material. Any poly-atomic system can be viewed as an intermixture of two coupled subsystems, constituted by M nuclei and N electrons respectively. In principle, the only prerequisite for the description of all the quantum mechanical properties of such a system, for simplicity in the non-relativistic regime, is the solution of the many-body Schrödinger equation