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Nanostructures: Theory and Modelling

纳米结构 ——理论与模拟

〔法〕C. Delerue M. Lannoo



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纳米结构

纳米结构

——理论与模拟

作者：[美] 詹姆斯·H·范德瓦特



纳米科学技术大系

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Theory and Modelling

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内 容 简 介

纳米科学的进展正在越来越依赖计算与模拟。这取决于三个因素的结合:减小纳米物质的尺寸、增强计算机的能力、发展新的理论。本书主要介绍了纳米结构体系中电子结构、介电性质、光学转换、电学输运的基本物理概念、理论方法、重要实验结果及其理论分析与模拟计算,是一本较为系统的、有使用价值的理论专著。

本书对从事纳米科技多学科交叉领域的高年级本科生、研究生及相关的科研教学人员具有重要的参考价值。

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Preface

This book is an introduction to the theory of nanostructures. Its main objectives are twofold: to provide basic concepts for the physics of nano-objects and to review theoretical methods allowing the predictive simulation of nano-devices. It covers many important features of nanostructures: electronic structure, dielectric properties, optical transitions and electronic transport. Each topic is accompanied by a review of important experimental results in this field. We have tried to make the book accessible to inexperienced readers and it only requires basic knowledge in quantum mechanics and in solid state physics. Whenever possible, each concept is introduced on the basis of simple models giving rise to analytical results. But we also provide the reader with the more elaborate theoretical tools required for simulations on computers. Therefore, this book is intended not only for the students beginning in this field but also for more experienced researchers.

The context of the book is the rapid expansion of nano-technologies resulting from important research efforts in a wide range of disciplines such as physics, biology and chemistry. If much work is presently focusing on the elaboration, the manipulation and the study of individual nano-objects, a major challenge for nano-science is to assemble these objects to make new materials and new devices, opening the door to new technologies. In this context, as the systems become more and more complex, and because probing the matter at the nanoscale remains a challenge, theory and simulation play an essential role in the development of these technologies. A large number of simulation tools are already available in science and technology but most of them are not adapted to the nano-world because, at this scale, quantum mechanical descriptions are usually necessary, and atomistic approaches become increasingly important. Thus, one main objective of the book is to review recent progress in this domain. We show that *ab initio* approaches provide accurate methods to study small systems ($\lesssim 100$ – 1000 atoms). New concepts allow us to investigate these systems not only in their ground state, but also in their excited states and out of equilibrium. The domain of application of *ab initio* methods also becomes wider thanks to the decreasing size of the systems, to the increasing power of the computers and to novel algorithms. But these developments are by far not sufficient enough to cover all the needs, in particular when the number of atoms in the systems becomes large ($\gtrsim 100$ – 1000).

Thus, most of the problems in nano-science must be investigated using semi-empirical approaches, and *ab initio* calculations are used to test or to calibrate the semi-empirical methods in limiting cases. Therefore, an important part of the book is devoted to semi-empirical approaches. In particular, we present recent improvements which greatly enhance their predictive power.

Due to the huge existing literature in this field, we have limited our bibliography to what we believe are the most basic papers. It is also clear that we have not covered all the aspects. For example, we have omitted nanomagnetism which merits a book of its own.

The book is divided into eight chapters. Chapter 1 gives a general overview of the basic theoretical methods which allow an understanding of the electronic properties from condensed matter to molecules and atoms. We present *ab initio* descriptions of the electronic systems in their ground state, in particular those based on the density functional theory, and we review recent approaches dealing with one-particle and two-particle excitations. Then, semi-empirical methods are introduced, from the simple effective mass approach to more elaborate theories such as tight binding and pseudopotential methods. Chapter 2 provides a general introduction to quantum confined semiconductor systems, from two to zero dimensions. We compare different computational techniques and we discuss their advantages and their limits. The theoretical predictions for quantum confinement effects are reviewed.

Chapter 3 deals with the dielectric properties of nano-objects. Microscopic methods based on electronic structure calculations are presented. Screening properties in semiconductor nanostructures are analyzed using both macroscopic and microscopic approaches. The concept of local dielectric constant is introduced and we conclude by discussing the possibility of using the macroscopic theory of dielectrics in nano-systems. We also point out the importance of surface polarization charges at dielectric interfaces for Coulomb interactions in nanostructures.

In Chapter 4, we focus on the description of quasi-particles and excitons, starting from the simpler methods based on the effective mass theory and progressing to more complex approaches treating dynamic electronic correlations. Chapter 5 discusses the optical properties of nanostructures. It begins with the basic theory of the optical transitions, concentrating on problems specific to nano-objects and including the influence of the electron-phonon coupling on the optical line-shape. The optical properties of semiconductor nanocrystals are then reviewed, both for interband and intraband transitions. Chapter 6 is devoted to hydrogenic impurities and point defects in nanostructures. In view of the importance of surfaces in small systems, surface dangling bond defects are discussed in detail. The chapter closes with study of self-trapped excitons showing that their existence is favored by confinement effects.

Non-radiative processes and relaxation mechanisms are considered in Chap. 7. The effect of the quantum confinement on the multi-phonon cap-

ture on point defects is studied. We present theoretical formulations of the Auger recombination in nanostructures and we discuss the importance of this mechanism by reviewing the experimental evidence. Then we address the problem of the relaxation of hot carriers in zero-dimensional objects. In strongly confined systems, phonon-assisted relaxation is slow due to the phonon bottleneck effect, but we explain why this effect is difficult to observe due to competitive relaxation mechanisms.

Chapter 8 discusses non-equilibrium transport in nanostructures. We introduce theoretical methods used to simulate current-voltage characteristics. We start with the regime of weak coupling between the nano-device and the electron leads, introducing the so-called orthodox theory. Situations of stronger coupling are investigated using the scattering theory in the independent particle approximation. Electron-electron interactions are then considered in mean-field approaches. The limits of these methods are analyzed at the end of the chapter.

Finally, we are greatly indebted to G. Allan for a long and fruitful collaboration. We are grateful to all our colleagues and students for discussions and for their contributions. We acknowledge support from the “Centre National de la Recherche Scientifique” (CNRS) and from the “Institut Supérieur d’Electronique et du Numérique” (ISEN).

Lille, Paris,
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C. Delerue
M. Lannoo

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1 General Basis for Computations and Theoretical Models

This chapter describes theoretical concepts and tools used to calculate the electronic structure of materials. We first present *ab initio* methods which are able to describe the systems in their ground state, in particular those based on the density functional theory. Introducing the concept of quasiparticles, we show that excitations in the systems can be accurately described as excitations of single particles provided that electron–electron interactions are renormalized by the coupling to long-range electronic oscillations, i.e. to plasmons. We then review the main semi-empirical methods used to study the electronic structure of nanostructures.

1.1 *Ab initio* One-Particle Theories for the Ground State

This section is an attempt to summarize the basic methods which have allowed an understanding of a wide range of electronic properties not only in condensed matter but also in molecules. The basic difficulty is due to the inter-electronic repulsions which prevent from finding any tractable solution to the general N electron problem. One is then bound to find approximate solutions. Historically most of these have tried to reduce this problem to a set of one-particle Schrödinger equations. Of course such a procedure is not exact and one must find the best one-particle wave functions via a minimization procedure based on the variational principle. This one is however valid for the ground state of the system and can only be applied exceptionally to excited states for which the total wave function is orthogonal to the ground state.

The general solution of the N electron system must be antisymmetric under all permutations of pairs of electron coordinates. We start by applying the constraint to the case of N non interacting electrons. We review on that basis the Hartree and Hartree–Fock approximations and give a qualitative discussion of correlation effects. We then pay special attention to the so-called density functional theories of which the most popular one is the local density approximation (LDA). These have the advantage of leading to a set of well-defined one-particle equations, much simpler to solve than in Hartree–Fock theory, and to provide at the same time fairly accurate predictions for

the ground state properties. We end up this section with a discussion of the meaning and accuracy of the one-particle eigenvalues for the prediction of excitation energies.

1.1.1 Non-interacting N Electron System

We start by discussing a hypothetical system of independent electrons for which the Hamiltonian can be written

$$H = \sum_{i=1}^N h(\mathbf{x}_i) , \quad (1.1)$$

where \mathbf{x}_i contains both space and spin coordinates ($\mathbf{x}_i = \mathbf{r}_i, \xi$). Each individual Hamiltonian $h(\mathbf{x}_i)$ is identical and has the same set of solutions:

$$h(\mathbf{x})u_k(\mathbf{x}) = \varepsilon_k u_k(\mathbf{x}) . \quad (1.2)$$

For such a simple situation the eigenstate ψ of H with energy E can be obtained as a simple product of one-electron states (also called spin-orbitals)

$$\psi = \prod_{k=1}^N u_k(\mathbf{x}_k) , \quad (1.3)$$

its energy being obtained as the sum of the corresponding eigenvalues:

$$E = \sum_{k=1}^N \varepsilon_k . \quad (1.4)$$

Although these solutions are mathematically exact they are not acceptable for the N electron system since ψ given by (1.3) is not antisymmetric. The way to solve this difficulty is to realize that any other simple product ψ_{kl} obtained from ψ by a simple permutation of \mathbf{x}_k and \mathbf{x}_l has the same energy E and is thus degenerate with ψ . The problem is thus to find the linear combination ψ_{AS} of ψ and all ψ_{kl} that is antisymmetric under all permutation $\mathbf{x}_k \leftrightarrow \mathbf{x}_l$. This turns out to be a determinant called the Slater determinant defined by:

$$\psi_{AS} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(\mathbf{x}_1) & \dots & u_1(\mathbf{x}_N) \\ u_2(\mathbf{x}_1) & \dots & u_2(\mathbf{x}_N) \\ \vdots & & \vdots \\ u_N(\mathbf{x}_1) & \dots & u_N(\mathbf{x}_N) \end{vmatrix} . \quad (1.5)$$

This determinant still has the energy given by (1.4). The ground state of the system is thus obtained by choosing for ψ_{AS} the N one-particle states u_i which have the lowest eigenvalues ε_k . However in doing this one must take care of the fact that the Slater determinant ψ_{AS} vanishes when two u_k are taken identical. This is the Pauli exclusion principle according to which two electrons cannot be in the same quantum state. If $h(\mathbf{x})$ is spin independent

the spin orbitals can be factorized as a product of a space part $u_k(\mathbf{r})$ and a spin part $\chi_\sigma(\xi)$

$$u_{k\sigma}(\mathbf{x}) = u_k(\mathbf{r})\chi_\sigma(\xi), \quad (1.6)$$

where \mathbf{r} is the position vector, ξ the spin variable and $\sigma = \uparrow$ or \downarrow . In such a case the Pauli principle states that two electrons can be in the same orbital state if they have opposite spin. The ground state of the system is thus obtained by filling all lowest one-electron states with two electrons with opposite spin per state.

1.1.2 The Hartree Approximation

The full Hamiltonian of the interacting N electron system is

$$H = \sum_k h(\mathbf{x}_k) + \frac{1}{2} \sum_{kk'} v(\mathbf{r}_k, \mathbf{r}_{k'}) + V_{\text{NN}}, \quad (1.7)$$

where the one-electron part h is the sum of the kinetic energy and the Coulomb interaction with the nuclei, v is the electron–electron interaction

$$v(\mathbf{r}_k, \mathbf{r}_{k'}) = \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}, \quad (1.8)$$

and V_{NN} is the Coulomb energy due to the interaction between the nuclei (throughout this chapter we use electrostatic units, i.e. $4\pi\epsilon_0 = 1$). It is of course the existence of the terms (1.8) which prevents from factorizing H and getting a simple solution as in the case of independent electrons. A first step towards an approximate solution to this complex problem came from the intuitive idea of Hartree [1–3] who considered that each electron could be treated separately as moving in the field of the nuclei plus the average electrostatic field due to the other electrons. This corresponds to writing an individual Schrödinger equation

$$\left[h(\mathbf{x}_k) + \sum_{k \neq k'} \int v(\mathbf{r}_k, \mathbf{r}_{k'}) |u_{k'}(\mathbf{x}_{k'})|^2 d\mathbf{x}_{k'} \right] u_k(\mathbf{x}_k) = \varepsilon_k u_k(\mathbf{x}_k) \quad (1.9)$$

for each of the N electrons of the system. To connect with the following we rewrite this equation in a more standard form

$$[h(\mathbf{x}) + V_{\text{H}}(\mathbf{x}) - \Sigma_k^{\text{SI}}(\mathbf{x})] u_k(\mathbf{x}) = \varepsilon_k u_k(\mathbf{x}) \quad (1.10)$$

which is obtained by adding and subtracting the term $k = k'$ in (1.9). $V_{\text{H}}(\mathbf{x})$ is the so-called Hartree potential, i.e. the electrostatic potential due to the total density $n(\mathbf{x})$ (including the term $k = k'$):

$$\begin{aligned} V_{\text{H}}(\mathbf{x}) &= \int v(\mathbf{r}, \mathbf{r}') n(\mathbf{x}') d\mathbf{x}', \\ n(\mathbf{x}) &= \sum_l n_l |u_l(\mathbf{x})|^2. \end{aligned} \quad (1.11)$$

The n_l introduced in the definition of $n(\mathbf{x})$ are the occupation numbers, $n_l = 1$ if there is an electron in u_l , $n_l = 0$ in the opposite case. The last term Σ_k^{SI} is the self-interaction correction, removing the unphysical term $k = k'$ introduced in the definition of V_H :

$$\Sigma_k^{\text{SI}}(\mathbf{x}) = \int v(\mathbf{r}, \mathbf{r}') |u_k(\mathbf{x}')|^2 d\mathbf{x}' . \quad (1.12)$$

The Hartree equations coupled with a spherical averaging of the potential in (1.10) have provided a quite accurate picture of the electronic structure of isolated atoms. They are a basis for understanding the periodic table of the elements and also produce good electron densities $n(\mathbf{x})$ as compared with those obtained experimentally from X-ray scattering.

The Hartree equations have been put on firm theoretical grounds by use of the variational principle [2, 4]. For this one takes as trial wave function ψ the simplest form one can obtain for independent electrons, without taking account of the antisymmetry. This one is thus the simple product of spin orbitals given by (1.3). The optimized ψ belonging to this family of wave functions must minimize the energy given by the expectation value of H for this wave function. This is equivalent to solving

$$\langle \delta\psi | E - H | \psi \rangle = 0 , \quad (1.13)$$

where $\delta\psi$ is an infinitesimally small variation of ψ . If one now varies each u_k separately in (1.13) by δu_k one directly gets the set of equations (1.9) or (1.10).

The Hartree method then succeeds in reducing approximately the N electron problem to a set of N one-particle equations. However the price to pay is that the potential energy in each equation (1.10,1.11) contains the unknown quantity $n(\mathbf{x}') - |u_k(\mathbf{x}')|^2$. One must then solve these equations iteratively introducing at the start some guess functions for the $|u_k|^2$ in the potential energy, solve the equations, re-inject the solutions for the $|u_k|^2$ (or some weighted averages) into the potential energy and so on (Fig. 1.1). The pro-

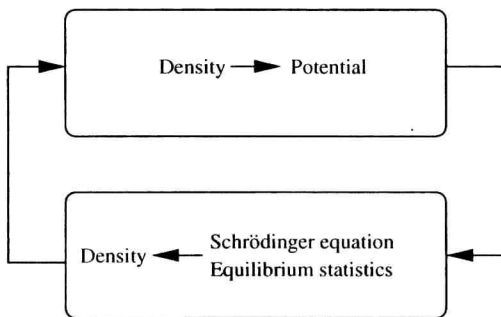


Fig. 1.1. The electron density and the potential must be calculated self-consistently taking into account the occupation of the levels

cedure stops when self-consistency, i.e. the identity between the input and output, is achieved.

1.1.3 The Hartree–Fock Approximation

This is less intuitive than the Hartree method and must be directly introduced from a variational treatment. The starting point is similar except that instead of choosing for ψ a simple product function one now makes use of Slater determinant of the form (1.5) in which the spin orbitals are assumed orthonormal. The total energy $E = \langle \psi | H | \psi \rangle$ of such a determinant can be shown [2, 3, 5, 6] to be given by

$$E = \sum_k n_k \langle k | h | k \rangle + \frac{1}{2} \sum_{k,l} n_k n_l (\langle kl | v | kl \rangle - \langle kl | v | lk \rangle) + V_{\text{NN}} \quad (1.14)$$

with:

$$\begin{aligned} \langle k | h | k \rangle &= \int u_k^*(\mathbf{x}) h(\mathbf{x}) u_k(\mathbf{x}) d\mathbf{x} , \\ \langle ij | v | kl \rangle &= \int u_i^*(\mathbf{x}) u_j^*(\mathbf{x}') v(\mathbf{r}, \mathbf{r}') u_k(\mathbf{x}) u_l(\mathbf{x}') d\mathbf{x} d\mathbf{x}' . \end{aligned} \quad (1.15)$$

We want to minimize E with respect to the u_k under the constraint that these remain orthonormal, i.e. $\int u_k^*(\mathbf{x}) u_l(\mathbf{x}) d\mathbf{x} = \delta_{kl}$. This can be achieved via the method of Lagrange multipliers. If we apply a first order change δu_k^* this requires that the quantity $\delta E - \sum_{kl} \lambda_{kl} \int \delta u_k^*(\mathbf{x}) u_l(\mathbf{x}) d\mathbf{x} = 0, \forall \delta u_k^*$. This leads to the set of one-particle equations:

$$\begin{aligned} & \left[h(\mathbf{x}) + \sum_l n_l \int v(\mathbf{r}, \mathbf{r}') |u_l(\mathbf{x}')|^2 d\mathbf{x}' \right] u_k(\mathbf{x}) \\ & - \sum_l n_l \left[\int v(\mathbf{r}, \mathbf{r}') u_l^*(\mathbf{x}') u_k(\mathbf{x}') d\mathbf{x}' \right] u_l(\mathbf{x}) = \sum_l \lambda_{kl} u_l(\mathbf{x}) . \end{aligned} \quad (1.16)$$

This can be simplified by noticing that a unitary transformation applied to the Slater determinant does not modify it apart from a phase factor and thus does not change the structure of the equations. It is thus possible to rewrite (1.16) under diagonal form, i.e. with:

$$\lambda_{kl} = \varepsilon_k \delta_{kl} . \quad (1.17)$$

For obvious reasons, the last term on the left hand side of (1.16) is called the exchange term, the second one being the Hartree potential V_{H} . We now rewrite (1.16) using (1.17) under a form which will be generalized in the following:

$$[h(\mathbf{x}) + V_{\text{H}}(\mathbf{x})] u_k(\mathbf{x}) + \int \Sigma_{\text{x}}(\mathbf{x}, \mathbf{x}') u_k(\mathbf{x}') d\mathbf{x}' = \varepsilon_k u_k(\mathbf{x}) , \quad (1.18)$$

Σ_x corresponding to the non-local exchange potential:

$$\Sigma_x(x, x') = -v(r, r') \sum_l n_l u_l(x) u_l^*(x'). \quad (1.19)$$

The $l = k$ term in (1.19) when injected into (1.18) directly corresponds to the self-interaction Σ_k^{SI} of (1.12). The Hartree-Fock (HF) procedure thus reproduces the Hartree equations plus corrective exchange terms for $l \neq k$.

When the spin orbitals are factorized as in (1.6) one can perform the integration over the spin variables directly in the HF equations. In that case the result is that the integrations over x' can be replaced by integrations over r' at the condition of multiplying V_H by a factor 2 for spin degeneracy while the exchange term remains unchanged since opposite spins give a vanishing contribution to (1.16).

While the HF approximation improves over the Hartree one, especially for magnetic properties, it does not provide an accurate enough technique for the ground state properties as well as the excitation energies. This is due to correlation effects which are important in both cases as will be discussed in the following. Furthermore HF leads to heavy calculations due to the non-local character of the exchange term.

1.1.4 Correlations and Exchange-Correlation Hole

By definition correlation effects are the contributions not included in the HF approximation. Conceptually the simplest way to include them is to use the method of configuration interaction (CI). The principle of the CI technique is to expand the eigenstates of the interacting N electron system on the basis of the Slater determinants built from an infinite set of orthonormal one-particle spin orbitals :

$$\psi = \sum_n c_n \psi_{SD,n}. \quad (1.20)$$

Quite naturally the starting point in such an expansion could be the ground state HF determinant, the others being built by substitution of excited HF spin orbitals. However the CI technique is quite heavy and does not converge rapidly so that it can be applied only to small molecules (typically 10 atoms maximum). This means that it cannot be applied to solids. We thus now discuss the only case where practically exact results have been obtained for infinite systems, i.e. the free electron gas.

The free electron gas is an idealized model of simple metals in which the nuclear charges are smeared out to produce a uniform positive background charge density. This one is fully compensated by the uniform neutralizing electron density. This produces a constant zero potential in all space. The solutions of the one-particle Hartree equations are