INTRODUCTION TO MODERN METHODS OF QUANTUM MANY-BODY THEORY AND THEIR APPLICATIONS

Editors

Adelchi Fabrocini
University of Pisa, Italy

Stefano Fantoni
National Institute for Advanced Studies, Italy

Eckhard Krotscheck
Johannes-Kepler University, Austria

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PREFACE

This volume of the series *Advances in Quantum–Many–Body Theories* contains the lecture notes of the second European summer school on *Microscopic Quantum Many–Body Theories and their Applications,* which was hosted during the time of Sept. 3– Sept. 14 by the Abdus Salam Center for Theoretical Physics in Miramare, Trieste (Italy). The aim of this school was to introduce a selected group of graduate students and young postdoctoral researchers to the dominant and most successful techniques of modern microscopic many–body theory. This summer school is the sequel of a preceding one that was held in September 1997 at the Universidad Internacional Menéndez Pelayo (UIMP) in Valencia. [a]

Modern quantum many-body theory (QMBT) had its birth some 50 years ago with the pioneering work of Brueckner, Gell–Mann, Feynman, Landau, Noziéres, Pines, to name only a few. It has since grown to become one of the most fundamental and exciting areas of modern theoretical physics. Its aims are to understand and predict those properties of macroscopic matter that have their origins in the underlying interactions between, and the quantum-mechanical nature of, the elementary constituents at the most microscopic level relevant to the energy range under consideration. The field is naturally multi–disciplinary within physics. Hence, QMBT has become an essential tool for researchers working in several, and apparently different, fields of physics, chemistry, and other disciplines. Among the specific areas of application we may count condensed matter; nuclear and high-energy physics; dense matter astrophysics; atoms and molecules; and elementary particles.

The variety of current approaches to the microscopic many-body problem includes density functional theory, the hypernetted chain/correlated basis functions formalism, the coupled cluster method, and numerical simulation methods. An important point that must be stressed is that the rapid evolution of the different formulations of QMBT over the last decade has provided valuable new insights regarding their intimate interrelationships. An appreciation of this underlying identity will surely provide students and researchers with a much deeper understanding of the physical content of QMBT itself and will offer a broader variety of practical theoretical tools. In this sense, familiarity with the basics of many-body theories should be part of the background knowledge of many researchers.

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[a] *Microscopic Quantum Many–Body Theories and their Applications,* eds. J. Navarro and A. Polls, in "Lecture Notes in Physics" Vol. 510 (1998).

This book contains pedagogical introductions to the above–mentioned dominant techniques of modern many–body theory, leading up to today's front–line research. These techniques have their roots in the standard analytical methods of theoretical physics: perturbation theory, scattering theory, and stationarity principles. More-over, the interplay between these methods and the computational ones has led to fruitful and novel insights into the physics of many–particle systems that deserve to be brought to the attention of the students.

A series of lectures on numerical simulation techniques has been delivered by Gaetano Senatore. They followed relatively closely the published notes by D. Ceper-ley[b] and it was felt that this adequate reference material on the subject did not justify an independent re–writing.

Two aspects can be broadly distinguished in QMBT: the *methods* or *techniques* used to study QMB systems, and the *specific fields of application* as well as ex-perimental verifications. Mindful of these primary objectives, this volume contains also reviews on *modern developments* and the applications include hypersherical expansion methods, the theory of highly dynamic systems, as well as some key experiments that address questions containing direct challenges to many–body the-orists. The contributions by E. Arimondo and H. Godfrin are included; two more seminars were given by P. Martin on metallic clusters and A. F. G. Wyatt on quan-tum evaporation.

We have selected authors for all of the above subjects with particular care both on the basis of outstanding reputations in the fields they represent and of their recognized research experience and knowledge of generic many–body theory. This volume, together with the lecture notes of the Valencia school, addresses the striking lack of a related pedagogical literature that would allow researchers to acquire the requisite physical insight and technical skills. While trying to avoid too much overlap with the Valencia lecture notes, we have nevertheless tried to make the articles contained in this volume self–contained.

A. Fabrocini
S. Fantoni
E. Krotscheck

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[b]see, for example, http://archive.ncsa.uiuc.edu/Apps/CMP/papers/cep96b.ps and http://www.mcc.uiuc.edu/SummerSchool/David%20Ceperley/ceperley.pdfit

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Chapter 7 THEORY OF CORRELATED BASIS FUNCTIONS

DENSITY FUNCTIONAL THEORY

George F. Bertsch

Institute for Nuclear Theory
and Department of Physics and Astronomy
University of Washington Seattle WA 98195 USA
E-mail: bertsch@u.washington.edu

Kazuhiro Yabana

Institute of Physics
University of Tsukuba
Tsukuba 305-8577 Japan

Density functional theory is a remarkably successful theory of ordinary matter, despite its *ad hoc* origins. These lectures describe the theory and its applications starting from an elementary level. The practical theory uses the Kohn-Sham equations, well-chosen energy functionals, and efficient numerical methods for solving the Schroedinger equation. The time-dependent version of the theory is also useful for describing excitations. These notes are based on courses given by one of the authors (GFB) at the Graduiertenkolleg in Rostock, Germany in March 2001 and the Summer School on Microscopic Quantum Many-Body Theories in Trieste, Italy in September 2001.

1. Introduction

The density functional theory is now widely applied in all areas of physics and chemistry, wherever properties of systems of electrons need to be calculated. The theory is very successful in calculating certain properties–hence its popularity. This is reason enough for a student of theory to learn what it is all about. However, it is quite different in philosophy to other many-body approaches that you will hear about. The tried-and-true path in theoretical physics is to look for systematic expansions for calculating the properties of interest, finding controlled approximations that be refined to achieve greater accuracy. The density functional theory is not at all systematic, and in the end its justification is only the quality of its predictions. However, it is rightly described as an *ab initio* framework, giving theories whose parameters are determined *a priori* by general considerations. These lectures will present the theory and its applications at a pace that I hope is understandable with a minimum of prior formal training in advanced quantum mechanics. In the first

lecture today, I will set the stage by deriving Hartree-Fock theory, presenting some results on the homogeneous electron gas, and finally presenting the Hohenberg-Kohn theorem, which has motivated the density functional approach.

I will begin the next lecture with a simple example of a density functional theory which can be worked out, ending up with the Thomas-Fermi theory of many-electron systems. Unfortunately, the Thomas-Fermi theory has very limited validity, and it has not been possible to make useful improvements despite many attempts. The DFT became useful only after Kohn and Sham introduced electron orbitals into the functional. In their theory the variables are the single-particle wave functions of electrons in occupied orbitals as well as the electron density. The theory then has a structure very close to mean-field theories such as the Hartree theory. The emphasis on using the density variable wherever possible leads directly to a version of the theory called the Local Density Approximation (LDA). The LDA is a significant improvement over Hartree-Fock (in ways we shall discuss), but at the same time one can see deficiencies inherent in that scheme. A more complicated implementation of the theory, called the Generalized Gradient Approximation, makes it surprising accurate for calculating structures and binding energies, and in this form the theory is widely applied.

The Kohn-Sham theory requires solving the 3-dimensional Schroedinger equation many times, and questions of algorithms and numerical methods are important in making applications of the theory. There are several well-developed methods to solve the equations, and each has its advocates. In my third lecture I will discuss some of these numerical aspects. I will also survey some of the applications, noting where the DFT is reliable and where its accuracy is problematic. I will also mention some directions that have been taken to make more accurate theories, going beyond the DFT.

All of this so far is a theory of matter in its ground state. We are of course also very interested in the excitations of many-body systems, and the DFT can also be applied to dynamics, where it is called time-dependent density functional theory (TDDFT). In my fourth lecture I will derive the equations to be solved and the algorithms used to solve the equations. The time-dependent theory is quite computationally intensive, and much progress can be made by finding more efficient numerical techniques. Finally, in the last lecture, I will show you some state-of-the-art applications of the TDDFT.

Although it is not really necessary for my lectures, I will use a second-quantized field operator notation because it is the most efficient way to write down expectation values in many-particle spaces. Let us start with the basic Hamiltonian, which can be taken as the sum of three terms,

$$H = \int d^3r \frac{\hbar^2}{2m} \nabla \psi^\dagger(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r'}|} \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r'}) \psi(\mathbf{r'}) \psi(\mathbf{r})$$

$$+ \int d^3r V_{ext}(\mathbf{r}) \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}). \tag{1.1}$$

The terms represent the electron kinetic energy, the electron-electron interaction, and the interaction of the electrons with an external field, respectively. The $\psi^\dagger$ and ψ are field operators with the Fermion anticommutation relations, $\{\psi^\dagger(\mathbf{r}), \psi(\mathbf{r}')\} = \delta(\mathbf{r} - \mathbf{r}')$. I will explain what one needs to know about these as we go along. As a warm-up to the theory, I will derive the Hartree-Fock theory. But before that, some issues of notation and units should be clarified.

1.1. *Units and notation*

In eq. 1.1 we used units in which e^2 has dimensions of energy-length. If you are used to the MKS system, you can convert formulas by the substitution $e^2 \rightarrow e^2_{MKS}/4\pi\epsilon_0$. One often sees formulas quoted in atomic units, with no explicit dimensional quantities. In atomic units, lengths are expressed in units of the Bohr, $a_0 = \hbar^2/me^2 = 0.529..$ Å and energies in units of the Hartree, $e^2/a_0 = 27.2.$ eV. Confusingly, one also sees energies quoted in Rydbergs, $e^2/2a_0 = 13.6..$ eV. Personally, I do not care for implicit atomic units because they hide the functional dependence on mass and charge. It is also common to express densities in terms of the parameter r_s, defined as the radius in atomic units of a sphere whose volume is the reciprocal density. Thus $r_s = (3n/4\pi)^{1/3}\hbar^2/me^2$, where n is the density of electrons. In presenting numerical results, I will often use "practical atomic units", taking eV for energy and Å (0.1 nm) for length.

1.2. *Hartree-Fock theory*

Hartree-Fock theory is very simple to describe: it is the variational theory obtained by the expectation value of the Hamiltonian, allowing all wave functions that can be represented as Slater determinants. Let's see how this comes about. Using second-quantized notation, the Slater determinants constructed from a set of orthonormal single-particle wave functions $\{a\}$ are represented by a product of creation operators $c^\dagger$ acting on the vacuum. An N-particle state is thus

$$|N\rangle = \sum_a^N c_a^\dagger |\rangle.$$

The operators $c\dagger$ and c satisfy the anticommutation relation $\{c_a^\dagger, c_{a'}\} = \delta_{a,a'}$. To get back the orbital wave function in position space, i.e. to reveal the spatial wave function $\phi_a(r)$, we apply the field operator $\psi(\mathbf{r})$ to the state a. The anticommutator gives the sought amplitude,

$$\{\psi(\mathbf{r}), c_a^\dagger\} = \phi_a(\mathbf{r}).$$

We now take the expectation value of H in the state $|N\rangle$ and reduce the operator expectation values by moving annihilation operators to the right and creation operators to the left with the help of the above anticommutators. The result at the

end is

$$\langle N|H|N\rangle = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla \phi_a^* \cdot \nabla \phi_a + \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\phi_a|^2|\phi_b|^2$$

$$- \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r}) + \sum_a \int d^3r V_{ext}(\mathbf{r})|\phi_a|^2. \quad (1.2)$$

The result looks very similar to eq. (1.1) with respect to the kinetic energy and the external potential energy terms. But the electron-electron interaction has given rise to two terms, the direct (or Hartree) energy, and the exchange (or Fock) energy. Notice also that the factor of 1/2 in eq. (1.1) has disappeared; instead one has a double sum over the $N(N-1)/2$ orbital pairs (a, b). It is often convenient to rewrite eq. (1.2) rearranging the sums slightly. Let us add terms with $a = b$ to the direct and exchange sums. This won't affect the result, because the direct and exchange cancel if the two orbitals are the same. The direct term can then be written as an independent sum over the a and b orbitals. Defining the single particle density $n(\mathbf{r}) = \langle N|\psi^\dagger(\mathbf{r})\psi(\mathbf{r})|N\rangle = \sum_a^N |\phi_a(r)|^2$, the direct and external field terms are seen to depend directly on $n(r)$. The full expectation value becomes

$$\langle N|H|N\rangle = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla \phi_a^* \cdot \nabla \phi_a + \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r})n(\mathbf{r}')$$

$$- \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r})$$

$$+ \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}). \quad (1.3)$$

Now that we have the Hartree-Fock energy function, the next task is to find the minimum within the allowed variational space. First let us recall quickly how variational principles work. If we have a integral expression $\int F(\phi)dx$ that depends on a function $\phi(x)$, the condition that the value is stationary with respect to variations in ϕ is

$$\frac{dF}{d\phi} = 0. \quad (1.4)$$

This must be satisfied for all values of x. If there is a constraint that some other integral $\int G(\phi)dx$ has a fixed value, the stationary condition contains the constraint as a Lagrange multiplier,

$$\frac{dF}{d\phi} + \mu\frac{dG}{d\phi} = 0. \quad (1.5)$$

We now apply this to the Hartree-Fock energy, eq. (1.2), varying with respect to a wave function amplitude ϕ_a^*. Remembering that the wave functions were assumed to be normalized, we impose the constraint $\int \phi_a^* \phi_a d^3r = 1$ with a Lagrange multiplier. The multiplier will be denoted ϵ_a; it looks exactly like the energy in the Schrödinger equation. The wave functions also have to be orthogonal as well, but it turns out

Table 1. Atomization energies of selected molecules

	Li_2	C_2H_2	20 simple molecules (mean absolute error)
Experimental	1.04 eV	17.6 eV	-
Theoretical errors:			
Hartree-Fock	-0.94	-4.9	3.1
LDA	-0.05	2.4	1.4
GGA	-0.2	0.4	0.35
τ	-0.05	-0.2	0.13

that it is not necessary to put in Lagrange multipliers to satisfy that condition. There is one more technical point in carrying out the variation. When the gradient of a function is varied, one first integrates by parts to move the gradient elsewhere in the expression. One must impose suitable boundary conditions on the function to carry out the integration by parts, and that must be remembered in solving the differential equations that result from the variation.

Without going through the steps I will just quote the result here. One obtains N equations for the amplitudes ϕ_a,

$$-\frac{\hbar^2}{2m}\nabla^2\phi_a(\mathbf{r}) + \int \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}')d^3r'\phi_a(\mathbf{r}) - \sum_b \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r})$$
$$+ V_{ext}(\mathbf{r})\phi_a(\mathbf{r}) = \epsilon_a\phi_a(\mathbf{r}). \tag{1.6}$$

These are the Hartree-Fock equations. It is interesting to see how well they do in making a theory of matter. In Table I is shown some energies calculated with eq. (1.6), taken from Refs. 1, 2. The entries in the table are atomization energies, which is the energy require to pull the cluster or molecule apart into individual atoms. Results are given for a simple atomic cluster, a simple molecule, and a set of molecules that are used as a testing ground for better theories. The mean absolute error in the atomization energies (energy difference between the molecule and the individual atoms in isolation) is 3 eV in the Hartree-Fock theory. The predicted binding of the Li_2 clusters is a factor ten too low, and another alkali metal cluster not in the table, Na_2, is incorrectly predicted to be unbound. We conclude that on a practical level Hartree-Fock is not accurate enough to be useful for chemistry or for computing cluster structures.

1.3. *Homogeneous electron gas*

We will see next time that the density functional theory makes use of the properties of the homogeneous interacting electron gas, and it will be useful to have on hand some analytic results. There is a systematic expansion of the energy of an electron gas accurate at high density. The first two terms are contained in the Hartree-Fock theory. They are the kinetic energy of a free Fermi gas, and its exchange energy. As part of the warmup, I will now derive them.