

0413.1-53
M626
1997

Series on Advances in Quantum Many-Body Theory — Vol. 7

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



E200301812



World Scientific

New Jersey • London • Singapore • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

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

Copyright © 2002 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 981-238-069-8

Printed in Singapore by Mainland Press

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

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, Nozières, 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.

^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. Moreover, 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. Ceperley^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 experimental verifications. Mindful of these primary objectives, this volume contains also reviews on *modern developments* and the applications include hyperspherical expansion methods, the theory of highly dynamic systems, as well as some key experiments that address questions containing direct challenges to many-body theorists. 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 quantum 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.

The school was facilitated by a grant from the European Community (HPCF-CT-1999-00197) as well as support from the ICTP and SISSA. The organizers would like to thank Mrs. Doreen Saulek for her efficient and courteous management.

A. Fabrocini
S. Fantoni
E. Krotscheck

^bsee, for example, <http://archive.ncsa.uiuc.edu/Apps/CMP/papers/cep96b.ps> and <http://www.mcc.uiuc.edu/SummerSchool/David%20Ceperley/ceperley.pdf>

CONTENTS

PREFACE	xi
Chapter 1 DENSITY FUNCTIONAL THEORY	1
1. Introduction	1
1.1. Units and notation	3
1.2. Hartree-Fock theory	3
1.3. Homogeneous electron gas	5
1.3.1. Free electrons	6
1.3.2. Exchange energy	7
2. What is density functional theory?	8
2.1. Hohenberg-Kohn theorem	8
2.2. A simple example: the Thomas-Fermi theory	9
2.2.1. Variational equation of Thomas-Fermi theory	10
2.2.2. Thomas-Fermi atom	10
2.2.3. An example	12
3. Kohn-Sham theory	13
3.1. Local density approximation	13
3.2. Spin and the local spin density approximation	14
3.3. The generalized gradient approximation	15
4. Numerical methods for the Kohn-Sham equation	16
4.0.1. Exact exchange	20
4.0.2. $\mathcal{O}(N)$ methods	20
5. Some applications and limitations of DFT	21
5.1. Two examples of condensed matter	21
5.2. Vibrations	22
5.3. NMR chemical shifts	23
6. Limitations of DFT	24
7. Time-dependent density functional theory: the equations	25
7.1. Optical properties	27
7.1.1. f -sum rule	28
7.2. Methods to solve the TDDFT equations	29
7.2.1. Linear response formula	31
7.3. Dynamic polarizability	32
7.4. Dielectric function	33

8. TDDFT: numerical aspects	34
8.1. Configuration matrix method	35
8.2. Linear response method	36
8.3. Sternheimer method	37
8.4. Real time method	37
9. Applications of TDDFT	39
9.1. Simple metal clusters	39
9.2. Carbon structures	41
9.3. Diamond	42
9.4. Other applications	44
9.5. Limitations	45
References	46

Chapter 2 MICROSCOPIC DESCRIPTION OF QUANTUM LIQUIDS

	49
1. Introduction	49
1.1. General properties	51
2. Microscopic description	54
3. Hypernetted-chain equations	63
3.1. Results for liquid ^4He	75
4. Minimization of the energy: Optimal two-body correlation functions	81
4.1. Asymptotic behavior	85
5. Low excited states	87
6. A ^3He impurity in liquid ^4He	93
6.1. The ^3He impurity as a probe in liquid ^4He	97
6.2. The excitation spectrum of the ^3He impurity	98
6.3. Correlated perturbative approach	99
7. Variational description of Fermi systems	102
7.1. Diagrammatic rules and Fermi hypernetted chain equations	109
7.2. Results for ^3He	112
7.3. Excited states and the dynamic structure function	114
8. Summary	116
9. Acknowledgments	117
References	118

Chapter 3 THE COUPLED CLUSTER METHOD AND ITS APPLICATIONS

	121
1. Introduction	122
2. The Coupled Cluster formalism	123
2.1. The exponential form of the wave function	123
2.2. The Configuration Interaction Method (CIM)	126
2.3. The Coupled Cluster equations	129
2.4. The reference state	131

2.5. The Bra Ground state	133
3. Approximation schemes	134
3.1. The SUB(n) or CCn approximation	134
3.2. Applications to Coulomb interacting systems	138
3.3. The HCSUB(n) approximation	142
4. Applications to light nuclei	143
4.1. The TICC2 approximation in configuration representation	145
4.2. TICC2 in coordinate representation	150
4.3. The nuclei ^4He and ^{16}O in the TICI2 approximation	156
4.4. Beyond TICI2	161
5. Helium droplets	163
5.1. The J-TICI3 approximation	164
5.2. Ground state of ^4He droplets	166
5.3. Collective states of ^4He droplets	168
5.4. ^3He droplets	173
References	176

Chapter 4 EXPERIMENTS WITH A RUBIDIUM BOSE-EINSTEIN CONDENSATE

	179
1. Introduction	179
2. Micromotion	181
3. BEC in 1D optical lattice	182
4. Condensate photoionization	186
5. Conclusions and acknowledgments	188
References	188

Chapter 5 THEORETICAL ASPECTS OF BOSE-EINSTEIN CONDENSATION

	191
1. Bosons and condensation	191
2. BEC in ^4He	194
3. BEC in dilute systems	197
4. Conclusions	201
5. Acknowledgments	202
References	202

Chapter 6 ELEMENTARY EXCITATIONS AND DYNAMIC STRUCTURE OF QUANTUM FLUIDS

	205
1. Introduction	205
2. Ground state of a quantum Bose fluid	208
2.1. Optimized ground state	208
2.2. Euler equation with the Jastrow wave function	210
3. Equation of motion method	214
3.1. Linear response	214

3.2. Time-dependent correlation functions	216
3.3. Action integral	217
3.4. Least action principle	218
3.5. Many-particle densities and currents	219
3.6. One- and two-particle continuity equations	220
4. Solving the continuity equations	221
4.1. Feynman approximation	222
5. CBF-approximation	224
5.1. Convolution approximation	225
5.2. Two-particle equation	226
5.3. One-particle equation	228
5.4. The self-energy and the linear response function	229
5.4.1. Numerical evaluation of the self-energy	230
5.5. Analytic structure of the self-energy	231
5.5.1. Anomalous dispersion in liquid ^4He	233
5.5.2. Absolute minimum in the spectrum	234
5.6. Dynamic structure function in the CBF-approximation	236
5.7. Summary	239
6. The full solution	239
6.1. Continuity equations	239
6.2. Continuity equations in momentum space	242
6.3. Phonon-roton spectrum	244
6.4. Sum rules	246
6.5. Results on two-particle currents	250
6.6. Precursor of the liquid-solid transition	251
7. Dynamics of a single impurity	253
7.1. Continuity equations	253
7.2. Linear response and self-energy	257
7.3. Hydrodynamic effective mass	260
8. Summary	262
References	262

Chapter 7 THEORY OF CORRELATED BASIS FUNCTIONS

	265
1. Introduction	265
2. Basics of CBF theory	268
2.1. Motivations, basic concepts, and definitions	268
2.2. Finite-order correlated basis functions theory	271
3. Techniques for matrix elements	272
3.1. Definitions and notations	272
3.2. Techniques for matrix elements. I. Diagonal quantities	275
3.3. Techniques for matrix elements. II. Off-diagonal quantities	278
4. Interpretation of effective interactions	283

4.1. Quasiparticle interaction	283
4.2. Variational BCS theory	289
4.3. CBF, the optimization problem, and momentum-dependent correlations	295
5. Infinite order CBF theory	298
5.1. Introduction	298
5.2. Correlated coupled cluster theory	299
5.3. CBF ring diagrams	308
6. Dynamics in correlated basis functions	315
6.1. Equations of motion for correlated states	317
6.2. Coherence and the Feynman theory of excitations	319
6.3. Diagrammatic reduction	320
6.4. Local approximations	322
6.5. Averaged CRPA equations	324
6.6. Response function and dynamic structure function	325
References	326

Chapter 8 THE MAGNETIC SUSCEPTIBILITY OF LIQUID ^3He

	329
1. Introduction	329
2. The susceptibility of bulk liquid ^3He	330
3. Liquid ^3He confined in aerogel	334
4. Two-dimensional liquid ^3He	335
5. Conclusions	337
6. Acknowledgements	337
References	337

Chapter 9 THE HYPERSPHERICAL HARMONIC METHOD: A REVIEW AND SOME RECENT DEVELOPMENTS

	339
1. Introduction	339
2. Microscopic systems	341
3. Jacobi coordinates	342
4. Hyperspherical coordinates	345
5. Hyperspherical functions	347
6. The coupled equations	351
7. The hyperspherical harmonic expansion in momentum space	352
8. Results for the $A = 3, 4$ nuclei with the hyperspherical harmonic expansion	354
9. Modified hyperspherical harmonic expansions	356
9.1. The potential basis	357
9.2. The correlated expansion	357
9.3. The adiabatic approximation	360

9.4. The extended hyperspherical harmonic expansion	361
9.5. Application of the EHH expansion to the helium atom	362
10. Variational calculations for three- and four-nucleon scattering processes	365
10.1. $N - d$ scattering	365
10.2. Results for the $N - d$ scattering	367
10.3. Results for the low energy $n - {}^3H$ and $p - {}^3He$ scattering	368
11. Electro-weak reaction on few-nucleon systems	369
11.1. The $p - d$ radiative capture	370
11.2. The hep reaction	371
12. Conclusions	374
References	376
 Chapter 10 THE NUCLEAR MANY-BODY PROBLEM	 379
1. Introduction	379
1.1. The nuclear interaction	381
1.2. Quantum simulations	383
1.3. Plan of the paper	385
2. The Hamiltonian	385
2.1. Two-body potential	385
2.2. Three-body interaction	387
3. The AFDMC method	388
3.1. The auxiliary field breakup for a v_6 two-body potential	389
3.2. Break-up for the three-body potential	389
3.3. The spin-orbit propagator	390
3.4. Trial wave function and path constraint	391
3.5. Tail corrections	393
3.6. The AFDMC algorithm	393
3.7. Finite size effects: The periodic box FHNC method	395
4. AFDMC applications to nucleon matter	396
4.1. Equation of state of neutron matter	396
4.2. Symmetry energy of nuclear matter	399
4.3. Spin susceptibility of neutron matter	400
5. Outlook and Conclusions	402
References	405
 INDEX	 407

CHAPTER 1

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,

$$\begin{aligned}
 H = & \int d^3r \frac{\hbar^2}{2m} \nabla \psi^\dagger(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) \\
 & + \int d^3r V_{ext}(\mathbf{r}) \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}).
 \end{aligned} \tag{1.1}$$

The terms represent the electron kinetic energy, the electron-electron interaction, and the interaction of the electrons with an external field, respectively. The ψ^\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 $e^2 \rightarrow e_{MKS}^2/4\pi\epsilon_0$. One often sees formulas quoted in atomic units, with no explicit dimensional quantities. In atomic units, lengths are expressed in units of the Bohr, $a_0 = \hbar^2/me^2 = 0.529.. \text{ \AA}$ and energies in units of the Hartree, $e^2/a_0 = 27.2. \text{ eV}$. Confusingly, one also sees energies quoted in Rydbergs, $e^2/2a_0 = 13.6.. \text{ eV}$. 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 \AA (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 $\phi_a(\mathbf{r})$, 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

$$\begin{aligned} \langle N|H|N \rangle = & \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla \phi_a^* \cdot \nabla \phi_a + \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_a|^2 |\phi_b|^2 \\ & - \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) + \sum_a \int d^3r V_{ext}(\mathbf{r}) |\phi_a|^2. \end{aligned} \quad (1.2)$$

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 $n(\mathbf{r}) = \langle N|\psi^\dagger(\mathbf{r})\psi(\mathbf{r})|N \rangle = \sum_a^N |\phi_a(\mathbf{r})|^2$, the direct and external field terms are seen to depend directly on $n(\mathbf{r})$. The full expectation value becomes

$$\begin{aligned} \langle N|H|N \rangle = & \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla \phi_a^* \cdot \nabla \phi_a + \frac{1}{2} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') \\ & - \sum_{a<b} \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) \\ & + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}). \end{aligned} \quad (1.3)$$

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 an 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 ₂ H 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 ,

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

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 Li₂ clusters is a factor ten too low, and another alkali metal cluster not in the table, Na₂, 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.