Current Trends in Condensed Matter Physics

Proceedings of the International Centre
of Condensed Matter Physics Symposium

CURRENT TRENDS IN CONDENSED MATTER PHYSICS

Brasília, January 23-27, 1989

Editors
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World Scientific
Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.,
P O Box 128, Farrer Road, Singapore 9128
USA office: 687 Hartwell Street, Teaneck, NJ 07666
UK office: 73 Lynton Mead, Totteridge, London N20 8DH

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ISBN 9971-50-950-4

Printed in Singapore by JBW Printers & Binders Pte. Ltd.

FOREWORD

This volume presents an overview of some important topics in Condensed Matter Physics. The selection of papers was presented at the Symposium on "Current Trends in Condensed Matter Physics", held in Brasılia on January 23–27, 1989. The Symposium marked the inauguration of the International Centre of Condensed Matter Physics (ICCMP) of the University of Brasília. The ICCMP is an institute for theoretical research, appropriately set up to hold regular topical conferences, workshops and winter schools on recent advances in Condensed Matter Physics.

The book begins with a review on density functional theory, delivered by Sham. This paper is followed by a report on recent advances in the theory of freezing of Coulomb liquids by Tosi. An *ab initio* LCAO method for physisorption and chemisorption at metal surfaces is then presented by Flores, Criado-Sancho, Garcia-Vidal, and Martin-Rodero. In the next paper, Foglio discusses the application of perturbation methods for the Anderson model in intermediate valence compounds. A related paper on the Kondo lattice by Continentino, Japiassu and Troper initiates the contributions on superconductivity. This work is followed by the paper on electron-electron interactions in copper-oxide planes of high-T_c superconductors by Mahan. Chao, Wei, and Bartkowiak present a two-band model for hole dynamics in these materials, and Rojo, Balseiro, Avignon, and Alascio describe an extended Hubbard model approach for highly correlated copper oxides.

Subsequently, Salinas presents a Cayley tree model for systems with competitive interactions and spin glasses, while de Aguiar, Bosco, Martinez, and Goulart Rosa describe the Cayley tree one-state Potts model. Finally Stinchcombe ends up this volume with a review on scaling theory application for the dynamics of fractals, disordered systems, and quasicrystals.

We wish to acknowledge the important financial support we received from the Brazilian agencies FINEP, CNPq, CAPES, and from the Office of External Affairs of ICTP (Trieste). The assistance we had from Ms. M. Vittoria von Bülow and Fontayny Kleber from Brasília, and Dr. K. K. Phua and Ms. Kim Tan from World Scientific, for the preparation of this volume, is also greatly acknowledged.

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CONTENTS

Density Functional Theory: Past and Present

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Abstract

After a brief review of the fundamentals of the density functional theory and its wide-ranging applications, recent advances are discussed. These include the problems of the low-lying excited states, such as the band-gap in insulators and semiconductors and the Fermi surface in conductors, and the extension of the density functional theory to superconductors and to finite magnetic fields.

I. INTRODUCTION

It has been twenty-five years since the paper of Hohenberg and Kohn[1] which founded the field of the density functional theory. In that period, through the effort of many people in applying the theory to a wide range of systems, from atoms and molecules to solids and nuclear matter, the density functional theory has been established as a useful method for treating the many-body effects for the ground state of an inhomogeneous system. Yet, the density functional theory remains today a vibrant field of research. Applications are being tested for ever more exotic systems, including the copper oxides and the theory is being extended in several directions. Thus, my talk will comprise of a quick review of the established part of the theory and a discussion of the current research. The outline is as follows:

1. Fundamentals of the density functional theory.
2. A cursory survey of its many applications.
3. The band gap problem.
4. The Fermi surface problem.
5. The inhomogeneous superconductor.
6. High magnetic field.
7. What remains to be done.

II. WHAT IS DENSITY FUNCTIONAL THEORY?

The one-line answer is that it is many-body quantum mechanics for everybody. By expressing the ground state energy as a functional of the density, the theory reduces the many-body problem to an equivalent one-particle theory with all the many-body effects collected in an effective potential. In this form, simple and effective approximation for including the many-body effects can be devised.

A many-electron system has the Hamiltonian

$$H = T + V + U, \tag{1}$$

where T is the kinetic energy of the electrons, V is the potential energy due to the external potential $v(r)$, and U is the potential energy due to the Coulomb interaction between electrons. Consider the class of many-electron systems which have the same mass and Coulomb interaction between particles but which have different potentials $v(r)$ due to the nuclei. In principle, for this class of systems, the specification of an external potential $v(r)$ determines all the properties of a system, in particular the ground state energy and the ground state density distribution $n(r)$. We may say that the ground state density $n(r)$ is a functional of the potential $v(r)$. Hohenberg and Kohn's theorem proves that the converse is also true, namely that the potential is, apart from an arbitrary constant, uniquely determined by the density $n(r)$. The proof, by *reductio ad absurdum*, is simple, showing that no two potentials differing by more than a constant can correspond to the same density distribution.

Clearly, the theorem can be applied to more than the class of electron systems. It could be for a class of fermions or of bosons. In the way the theorem was stated above, clearly the mathematical niceties of the Banach spaces of $n(r)$ and of $v(r)$ are glossed over. A constructive procedure which avoids such problems to some extent was given by Levy.[2]

As a result of the Hohenberg-Kohn theorem, the ground state energy can be put in the form:

$$E = \int drn(r)v(r) + F[n(r)] \tag{2}$$

where the first term is the ground state expectation of V and F[n] is the expectation value of $T + U$. There is a variational theorem for the energy which says that for a given potential $v(r)$, the correct density put in the expression (2) yields the lowest energy. The functional derivative of Eq. (2),

$$\frac{\delta F}{\delta n} + v = \mu, \tag{3}$$

where μ is the chemical potential, then in principle determines the density distribution. This forms the basis of the gradient expansion of the density, the leading term being the Thomas-Fermi[3] approximation including the exchange-correlation effects.

Kohn and Sham[4] reduced the variational equation (3) to an equivalent one electron Schrödinger equation and, thus, rendered the solution for the density practical without the well-known shortcomings of the Thomas-Fermi approximation. Consider first a class of noninteracting electrons (i.e. with $U = 0$). The ground state energy can be written in the same form as Eq. (2) with $F[n]$ replaced by $T_s[n]$, which is the ground state kinetic energy of the non-interacting system with the density distribution $n(r)$. The variational equation becomes

$$\frac{\delta T_s}{\delta n} + v = \mu, \tag{4}$$

whose solution is the same as that of the one-electron Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + v(r)\right]\psi_j(r) = \varepsilon_j\psi_j(r), \tag{5}$$

yielding the density

$$n(r) = \sum_j \theta(\mu - \varepsilon_j)|\psi_j(r)|^2. \tag{6}$$

The point of the exercise is that, even though we might not know the explicit form[5] of the functional $T_s[n]$, the solution of the variational equation (4) is equivalent to solving a one-particle Schrödinger equation.

For the class of interacting electron systems, with U reinstated, we write

$$F[n] = T_s[n] + \frac{1}{2}\int dr \int dr' n(r)u(r-r')n(r') + E_{xc}[n]. \tag{7}$$

The first term is *not* the kinetic energy of the interacting system. The second term is the electrostatic energy due to the electron charge distribution, where $u(r)$ is the Coulomb interaction. The remainder may be termed the exchange-correlation energy, following the practice for the homogeneous electron gas. Equation (3) now has the same form as Eq. (4), except the potential $v(r)$ is replaced by

$$v_{eff}(r) = v(r) + \int dr' u(r-r') + v_{xc}(r). \tag{8}$$

The second term on the right is the electrostatic potential due to the electronic charge distribution. The third term is

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}, \tag{9}$$

which may be viewed as the exchange-correlation potential. In this manner, the many-body problem is reduced to the solution of the one-particle Schrödinger equation (5) with the effective potential v_{eff} in place of v.

The problem now becomes the construction of the exchange-correlation energy functional $E_{xc}[n]$. A simple approximation in the spirit of the Thomas-Fermi approximation is the local density approximation(LDA)[4]:

$$E_{xc} = \int dr \varepsilon_{xc}(n(r))n(r), \tag{10}$$

where $\varepsilon_{xc}(n)$ is the exchange-correlation energy per electron of the homogeneous gas at the density n. The exchange-correlation potential v_{xc} is then given by $\mu_{xc}(n)$, the exchange-correlation part of the chemical potential of the homogeneous electron gas at the local density n.

For finite systems and for magnetic systems, the spin degrees of freedom are important. The density functional theory is easily extended to the two spin-component density[4] and the corresponding LDA is now commonly known as local spin density approximation (LSD).

III. APPLICATIONS

There have been literally thousands of papers utilizing the density functional theory, particularly the LDA. Even the review articles and books are too numerous to quote here.[6,7] The following is a list of systems and their prominent properties which have been covered:

1. Atoms: Total energy, ionization potential and affinity.
2. Molecules: Stability of diatomic atoms. Be_2 is a particular example where Hartree-Fock predicted no binding, where an early configuration interaction calculation predicted weak binding but where LDA predicted binding[8,9] though too strong compared with the subsequent experiment.
3. Bulk solids: Cohesive energy, crystal structure, equilibrium lattice constant, elastic constants, phonon frequencies, Fermi surface, magnetization.
4. Point defects in solids: Determination of the atomic arrangement by comparison of total energy.
5. Surfaces: Structure and adsorption.
6. Space charge layers in semiconductors: Subband structure.

7. Nuclear matter: Density oscillations in a finite nucleus[10] and surface energy.[11]

8. Electron-hole drop: Surface.[12]

Here are a couple of opinions of the practitioners in the field who have found the theory useful:

- In a Letter on "Metal-metal bonding in Cr-Cr and Mo-Mo dimers" by the Northwestern group[13] which is an important center for electronic band structure studies, Delley et al. gave a subtitle "Another success of local spin-density theory" and said, "The local density functional theory is now the most widely used theoretical approach for determining the electronic structure of materials. Its great utility derives from the accurate experimental predictions obtained in systematic and extensive theoretical investigations of the electronic structure and properties of molecules and a wide variety of bulk solids and surfaces."
- Parr[14] in a review from the viewpoint of a theoretical chemist said, "Density functional theory will contribute substantially to the ultimate quantum-theoretical elucidation of chemistry."

To balance the favorable remarks, let me quote a couple of contrary opinions:

- Kryachko:[15] "... there still seems to be a misguided belief that a one-particle density can determine the exact N-body ground state."
- Lieb:[16] "... the universal functional is very complicated and essentially uncomputable."

In general, the LDA is adequate for the ground state properties, including changes due to variations of the atomic configuration or of the electron numbers, but the eigen-energies of Eq. (5) cannot always adequately represent the excited state properties. Thus, the ionization potential and the affinity energy calculated as total energy differences of N and $N \pm 1$ electron states are well given by LDA (or LSD) but

TABLE I. Si "ground state" properties

	Exp	Yin, Cohen	Bachelet et al.	Nielsen Martin	Harman Weber Hamann	Geöbel Segall Andersen
a_0	5.431 Å	0.5%	2%	-1%	1%	-0.5%
B	0.992 Mbar	-1%	3%	-6%	-12%	-1%
$\partial B/\partial P$	4.15	-20%		1%	-1%	
E_{coh}	4.63 eV	4%			5%	4%
C_{11}-C_{12}	1.025 Mbar	5%		-5%		
C_{44}	0.801 Mbar	—		6%		
$\omega_{LTO}(\Gamma)$	15.53 THz	-3%		-0.3%		
$\omega_{LO}(X)$	12.32	-3%				
$\omega_{TO}(X)$	13.90	-3%				
$\omega_{TA}(X)$	4.49	-3%				
$\gamma_{TO}(\Gamma)$	0.98	-8%				
$\gamma_{LO}(X)$	1.50	-13%				
$\gamma_{TO}(X)$	0.9	0				
$\gamma_{TA}(X)$	-1.4	-7%				

not always the case as the eigenvalues of the density functional Schrödinger equation (5) for the N particle system. Bulk solid semiconductors provide a good example. Table I shows the error of LDA calculations[17-21] for a list of "ground state properties" for silicon. The agreement appears to be excellent on the whole, considering that the only input is the electron gas $\mu_{xc}(n)$, the atomic number and the crystal lattice. The most striking example is shown by Fig. 1, the first-principles theory[17] of the total energies of various crystal structures of silicon under pressure. The theory not only was able to distinguish correctly the small difference between the diamond structure and the hexagonal diamond structure at room pressure but it predicted the

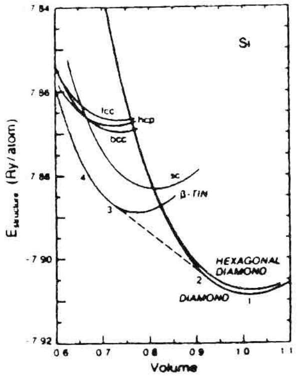

Figure 1: Total energy curves of various structures of silicon, taken from Fig. 5 of Ref. 17 by Yin and Cohen with permission of authors

transition under pressure to the β-tin structure, which was subsequently confirmed by experiment.

Against this background of success for the semiconductors, the uniform lack of agreement between LDA and experiment on the band gaps, as shown by Table II, is disturbing. Whether this is due to the inadequacy of the local density approximation (10) or due to the fact that the eigen-energies of the density function equation (5) do not represent the energies of the excited states is the band-gap problem which we shall address in the next section.

IV. THE BAND GAP PROBLEM

To solve the problem posed above, we need (1) a theory of the exchange-correlation potential beyond the LDA, (2) a precise theoretical understanding of the energy gap from the many-electron view-point and its relation to the density functional eigenvalues, and (3) numerical evaluations of the improvement over LDA and the band gaps from the exact definition for specific systems. All three steps have been taken and we believe we have a measure of understanding of the problem,

TABLE II. Energy gaps in semiconductors (Refs. 17, 18)

		Theory (eV)	Expt.	Diff.
Si				
	$\Gamma'_{25} - X_1(0.85)$	0.48	1.17	-0.69
	$\Gamma'_{25} - \Gamma_{15}$	2.54	2.74	-0.20
Ge				
	$\Gamma'_{25} - L$	0.47	0.74	-0.27
	$\Gamma'_{25} - \Gamma'_2$	0.73	0.89	-0.16
C				
	$\Gamma'_{25} - X_1(.85)$			
	$\Gamma'_{25} - \Gamma_{15}$	6.3	7.3	-1.0
GaAs				
	$\Gamma_v - \Gamma_c$	0.71	1.5	-0.79
	$\Gamma_v - X_1$	1.48	1.8	-0.32
GaP				
	$\Gamma_v - \Gamma_c$	1.87	2.33	-0.46
TiO_2		1.5	3	

although an interesting controversy over the relative importance of the improvement over LDA and the density functional eigen-values as approximation to the excited states remains.

LDA approximates the exchange-correlation effects by the corresponding terms of the homogeneous electron gas at the local density. Even though LDA has shown in practice to be good for a wide range of systems, one can imagine circumstances where it will fail. An example is the very localized and highly correlated f electrons in the heavy-electron metals.[22] Hybridization of the f-level with the d,p bands yields an f-band with a width of about 0.1 eV in LDA, which is about an order of magnitude larger than experiment. Yet, LDA[23] gives an excellent Fermi surface for the heavy electron metal $CeSn_3$. How to construct an exchange-correlation functional appropriate for the highly correlated electrons is an important and interesting challenge.

Improvement of LDA so far has involved either gradient corrections or special constructs which do not work universally well. A formal expression for $E_{xc}[n]$ has been given[24] in terms of the field theoretic perturbation theory using the Green's function constructed from the density function equation (5) as the starting point. The exchange-correlation potential $v_{xc}(r)$ is then given by an integral equation in terms of the exchange-correlation part of the self-energy. The solution of the integral equation is shown to have the correct asymptotic behavior for restricted systems such as atoms or metal surfaces. The potential can be obtained numerically beyond LDA once an approximation for the self-energy is decided, such as the random phase approximation (RPA). The LDA expression can also be derived from the integral equation. What is lacking is a simple approximation for the solution which combines the virtue of the LDA in the bulk region and which preserves the asymptotic behavior in the low density region. Since the most important error of LDA comes from the approximation to the exchange, a possible approach might be to separate the exchange from the correlation term. It must be pointed out that, in the context of the density functional theory, the separation is a matter of some controversy.

Do the eigenvalues ε_j from the effective one particle equation (5) with the exact exchange-correlation potential v_{xc} represent the energies of the excited states? The answer is no, in general. The highest occupied density functional eigen-energy does represent the chemical potential in the conductor case and the valence band edge in the insulator or semiconductor case. The band gap of an insulator or a semiconductor can be defined precisely in terms of the ground state energy as a function E_M of the number of particles M. If the insulating ground state has N particles, the conduction band edge is the change of the total ground state energy when an electron is added and the valence band edge is given by the change when an electron is removed:

$$E_c = E_{N+1} - E_N \tag{11}$$

$$E_v = E_N - E_{N-1}. \tag{12}$$

The band gap is naturally the difference:

$$E_g = E_c - E_v. \tag{13}$$

It is straightforward to show[25] from the definition of E_v and with the help of the variational theorem that the valence band edge is given by the highest occupied density functional eigen-energy:

$$E_v = \varepsilon_N. \tag{14}$$

Now, the Hohenberg-Kohn theorem is implicitly for a fixed number of electrons, M. Equation (5) and v_{xc} are implicitly defined as functions of M. Since $M = N$ gives the insulating ground state, we will argue below[25,26] that when an electron is removed, the highest occupied state is not changed much [only to $O(1/N)$] and $v_{xc}(N-1)$ is the same as $v_{xc}(N)$ but that when an electron is added across the gap, the $(N+1)$th state is very different and there is a discontinuity in v_{xc} as N is changed to $N+1$:

$$v_{xc}(N+1) = v_{xc}(N) + \Delta_{xc}, \tag{15}$$

where Δ_{xc} is independent of position. It follows that the difference between the true gap, Eq. (13) and the density functional gap given by

$$\varepsilon_g = \varepsilon_{N+1} - \varepsilon_N, \tag{16}$$

is just the potential discontinuity, Δ_{xc}.

There are a number of arguments for the existence of the discontinuity of v_{xc} across N. The first is that, from the chemical potential argument applied to Eq. (5) for the non-interacting and interacting systems respectively, $\delta T_s/\delta n$ has a discontinuity of ε_g and $\delta F/\delta n$ has a discontinuity of E_g across N. It would be the purest coincidence if the two functional derivatives have the same discontinuity. The second argument is that the discontinuity of v_{xc} can be expressed in terms of the self-energy.[25] The third argument, the strongest, is the explicit demonstration for a number of systems.

Consider the case of a proton with 0,1,2 electrons. The energy for introducing the first electron is $\varepsilon_1 = 1Ryd$ and the energy for added a second electron with the opposite spin is $\varepsilon_1 + U$, when the additional energy U is due to the Coulomb interaction between the two electrons. Thus, the density function gap is zero and the true gap and the v_{xc} discontinuity is U. This example may also be regarded as the atomic limit of the Hubbard model. Another example is a two-plane wave model in the Hartree-Fock approximation[25] and beyond.[27]

A more persuasive demonstration of the importance of the discontinuity is the calculation of the discontinuity for a number of semiconductors in RPA.[28] RPA for the Green's function using the LDA basis set[29] has been shown to give very good band structures for a number of semiconductors, including the band gaps. Godby et al.[28] calculated the density functional potential for a number of semiconductors, diamond, Si, GaAs, and AlAs, from the self-energy in RPA by iteration from the LDA. The Green's function in RPA is then calculated using the density functional single particle states and is used to determine the quasi-particle energies. The calculated band gaps are in very good agreement with experiment, as shown in