Electronic and Thermodynamic Properties of Transition Metal Elements and Compounds

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Abstract

This thesis focuses on the use of band-structure calculations for studying thermodynamic properties of solids. In a series of papers, we discuss 3d-, 4d- and 5d-transition metal carbides and nitrides. Through a detailed comparison between theoretical and experimental results, we draw conclusions on the character of the atomic bonds in these materials. We show how electronic structure calculations can be used to give accurate predictions for bonding energies, despite large absolute errors in theoretical results. Part of the thesis is devoted to the application of the generalized gradient approximation in electronic structure calculations on transition metals. Furthermore, we suggest two approximate approaches for studying thermal excitations. For structures with vibrational disorder, we present a method for calculating averaged phonon frequencies without using empirical information. For magnetic excitations, we show how a combined use of theoretical results and experimental data can yield information on magnetic fluctuations at high temperatures. The main results in the thesis are:

- Apart for an almost constant shift, theoretically calculated bonding energies for transition metal carbides and nitrides agree with experimental data or with values from analyses of thermochemical information.
- The electronic spectrum of transition metal carbides and nitrides can be separated into bonding, antibonding and nonbonding electronic states.
- The lowest enthalpy of formation for substoichiometric vanadium carbide VC_{1-x} at zero temperature and pressure occurs for a structure containing vacancies $(x \neq 0)$.
- The generalized gradient approximation improves theoretically calculated cohesive energies for 3d-transition metals. The same effect will probably be seen for 4d- and 5d-series elements if angular variations in the crystal potential are taken into account.
- Magnetic phase transitions are sensitive to the description of exchange-correlation effects in electronic structure calculations.
- Trends in Debye temperatures can be successfully analysed in electronic structure calculations on disordered lattices. For the elements, there is a clear dependence on the crystal structure (e.g., bcc, fcc or hcp).
- Chromium has fluctuating local magnetic moments at temperatures well above the Néel temperature.

Key words: Electronic structures, bonding theory, transition metal carbides and nitrides, density functional theory, magnetic phase transitions.

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This thesis focuses on the use of band-structure calculations for studying thermodynamic properties of solids. In a series of papers, we discuss $3d$-, $4d$- and $5d$-transition metal carbides and nitrides. Through a detailed comparison between theoretical and experimental results, we draw conclusions on the character of the atomic bonds in these materials. We show how electronic structure calculations can be used to give accurate predictions for bonding energies, despite large absolute errors in theoretical results. Part of the thesis is devoted to the application of the generalized gradient approximation in electronic structure calculations on transition metals. Furthermore, we suggest two approximate approaches for studying thermal excitations. For structures with vibrational disorder, we present a method for calculating averaged phonon frequencies without using empirical information. For magnetic excitations, we show how a combined use of theoretical results and experimental data can yield information on magnetic fluctuations at high temperatures. The main results in the thesis are:

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Preface

This thesis is divided into two parts. The first part is a brief introduction to the field of electronic structure calculations. It is intended to give a theoretical background to the material in the articles and a summary of the results in this thesis as well as in related works. The second part of the thesis contains eleven articles that have already been published, or which have been submitted for publication. These are:

1. J. Häglund, G. Grimvall, T. Jarlborg, and A. Fernández Guillermet
   Band structure and cohesive properties of 3d-transition-metal carbides and nitrides with the NaCl-type structure
   Phys. Rev. B **43**, 14400 (1991).

2. A. Fernández Guillermet, J. Häglund, and G. Grimvall
   Cohesive properties of 4d-transition-metal carbides and nitrides in the NaCl-type structure
   Phys. Rev. B **45**, 11557 (1992).

3. A. Fernández Guillermet, J. Häglund, and G. Grimvall
   Cohesive properties and electronic structure of 5d-transition-metal carbides and nitrides in the NaCl-type structure
   Submitted for publication.

4. J. Häglund, A. Fernández Guillermet, G. Grimvall, and M. Körling
   Theory of bonding in transition metal carbides and nitrides
   Submitted for publication.

5. J. Häglund, G. Grimvall, and T. Jarlborg
   Electronic structure, x-ray photoemission spectra, and transport properties of Fe_3C (cementite)
   Phys. Rev. B **44**, 2914 (1991).

6. V. Ozoliņš and J. Häglund
   First-principles study of effective cluster interactions and enthalpies of formation of substoichiometric VC_{1-x}
   Submitted for publication.

7. M. Hammar, C. Törnevik, J. Rundgren, Y. Gauthier, S. A. Flodström, K. L. Håkansson, L. I. Johansson, and J. Häglund
   Surface atomic structure of reconstructed $VC_{0.8}(111)$ studied with scanning tunneling microscopy
   Phys. Rev. B **45**, 6118 (1992).

8. M. Körling and J. Häglund
   Cohesive and electronic properties of transition metals: The generalized gradient approximation
   Phys. Rev. B **45**, 13293 (1992).

9. J. Häglund
   Fixed-spin-moment calculations on bcc and fcc iron using the generalized gradient approximation
   Phys. Rev. B **47**, 566 (1993).

10. J. Häglund, G. Grimvall, and T. Jarlborg
    An ab initio method for band-structure calculations on structurally disordered materials: vibrational properties of 4d transition metals
    Phys. Rev. B **47**, XXX (1993).

11. G. Grimvall, J. Häglund, and A. Fernández Guillermet
    Spin fluctuations in paramagnetic chromium from entropy considerations
    Submitted for publication.

Acknowledgments

Contents

Abbreviations

DOS	density-of-states
FSM	fixed-spin-moment
GEA	gradient expansion approximation
GGA	generalized gradient approximation
HF	Hartree-Fock
HS	high-spin
LAPW	linear augmented plane waves
LDA	local density approximation
LMTO	linear muffin-tin orbital
LS	low-spin
LSDA	local spin-density approximation
MT	muffin-tin
MTO	muffin-tin orbital
SIC	self-interaction correction

Chapter 1

Electronic interactions

1.1 Introduction

The physical behaviour of atoms, molecules and solids is often directly related to the effects of electronic interactions. Quantum mechanics shows how these interactions occur and how they should be treated. Thus, it is theoretically possible to determine energy levels of atoms, bond lengths and energies of molecules, lattice parameters and elastic constants of solids, and many other physical properties, without any other initial information than atomic numbers. Such an approach is often referred to as *ab initio*, which is Latin for "from the beginning". Evidently, an *ab initio* treatment of atoms, molecules and solids is appealing, both for theoretical and practical reasons.

A complete description of an N-electron system requires the knowledge of the total wave function, $\Psi(r_1, \ldots, r_N)$. Unfortunately, the problem of determining $\Psi(r_1, \ldots, r_N)$ grows very quickly with the number of electrons, N. In practice, N-electron wave functions can only be determined for very light atoms.

The possibility of a purely theoretical treatment of electronic systems has encouraged many physicists and chemists to suggest approximate *ab initio* methods. These efforts have been very successful and, with the advent of powerful computers, *ab initio* methods have become an important support, and sometimes even an alternative, to experimental studies. In the following paragraphs, we outline some of the major achievements in this field, and we summarize some of the theories that currently represent the state-of-the-art for describing electron-electron interactions.

1.2   The Hartree and Hartree-Fock approximations

A natural starting point for a discussion of electronic interactions is the Hartree approximation.[1] Historically, this also represents the first attempt to give a quantum mechanical description of an N-electron system. Hartree suggested that the total wave function can be approximated by a product of one-electron wave functions, $\Psi^{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\ldots\psi(\mathbf{r}_N)$. Further, he assumed that each electron moves in an electrostatic potential due to all other electrons, thus obeying a one-electron Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}^{i}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \tag{1.1}$$

where $V_{\text{ext}}(\mathbf{r})$ is an external potential and

$$V_{\text{H}}^{i}(\mathbf{r}) = e^2 \int \frac{n_i(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\,d\mathbf{r}', \tag{1.2}$$

$$n_i(\mathbf{r}) = \sum_{\substack{j=1 \\ i \neq j}}^{N} |\psi_j(\mathbf{r})|^2. \tag{1.3}$$

These equations yield a self-consistent scheme for determining $\psi_1 \ldots \psi_N$.

Although the Hartree approximation is important as a first step towards the description of a system of interacting electrons, it has some obvious shortcomings. The most important is that $\Psi^{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ does not obey the Pauli exclusion principle, i.e., it is not antisymmetric under interchange of electron indices. This lack is corrected in the Hartree-Fock (HF) approximation,[2] where the total wave function is written as a so-called Slater determinant of one-electron states

$$\Psi^{HF}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \psi_2(\mathbf{r}_N) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix}. \tag{1.4}$$

By minimizing the expectation value of the total Hamiltonian with respect to all antisymmetric wave functions, $\Psi^{HF}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, a Schrödinger equation for each $\psi_i(\mathbf{r})$ can be written,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{x}}^{i}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \tag{1.5}$$

where

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \, d\mathbf{r}', \tag{1.6}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \tag{1.7}$$

$$V_x^i(\mathbf{r}) = -e^2 \sum_{j=1}^{N} \int \frac{\psi_j(\mathbf{r}_j)\psi_i^\dagger(\mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|} \, d\mathbf{r}_j. \tag{1.8}$$

In Eq. (1.5), the *exchange potential*, $V_x^i(\mathbf{r})$, arises from the antisymmetry condition. We note that the Hartree potential in Eq. (1.6) includes an incorrect *self-interaction*, i.e., an apparent electrostatic repulsion between an electron and its own charge distribution. However, this term is cancelled by the exact exchange potential, $V_x^i(\mathbf{r})$ [Eq. (1.8)]. Although Eqs. (1.1) and (1.5) are formally similar, the solution of the one-electron HF equations is a much more difficult problem since $\psi_i(\mathbf{r})$ is implicit in $V_x^i(\mathbf{r})$. A detailed account of the Hartree-Fock approximation and its extensions has been given by Slater.[3]

In practice, the Hartree-Fock approximation represents a tedious but feasible way of obtaining the electronic states of light atoms and molecules. It gives an exact treatment of exchange effects but, in its simplest form [Eqs. (1.5)-(1.8)], it does not allow for other correlations in electronic movements. The fact that electrons will tend to avoid each other more than what is given by the Hartree potential [Eq. (1.6)] and by the exchange potential [Eq. (1.8)] will, in the following discussion, be attributed to *correlation effects*.

For solids, the HF approach is of much greater complexity than for atoms since the exchange integral in Eq. (1.8) has contributions from orbitals centered at an almost infinite number of lattice sites. Nevertheless, there are recent examples of successful HF calculations on solids.[4]

1.3 Density functional theory

Density functional theory provides a different approach to electronic structure determinations. The basic idea, originally suggested by Thomas[5] and Fermi,[6] is to use the electron density, $n(\mathbf{r})$, as a fundamental quantity instead of the N-electron wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Slater[7] showed that the exchange potential [Eq. (1.8)] can be approximated by $V_x(\mathbf{r}) \sim [n(\mathbf{r})]^{1/3}$. A theorem stating that the ground-state energy can be written as a unique functional of the electron density was proved by Hohenberg and Kohn.[8] Further, Kohn and Sham[9,10] presented a scheme for electronic structure determinations that is the basis of most modern methods for quantum-mechanical calculations on

atoms, molecules and solids. Recent reviews of results from density functional calculations are found in Refs. 11, 12 for atoms and molecules, and in Ref. 11 for solids.

Levy[13] has suggested an alternative view of density-functional theory, and a simplified proof of the Hohenberg-Kohn theorem. Following that approach, we define a total Hamiltonian of an interacting N-electron system,

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \int V_{ext}(\mathbf{r})\hat{n}(\mathbf{r})\,d\mathbf{r}, \tag{1.9}$$

where

$$\hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2, \tag{1.10}$$

$$\hat{V}_{ee} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1.11}$$

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{1.12}$$

are operators for kinetic energy, Coulomb energy and electron density, respectively. The ground-state energy is obtained by minimizing the expectation value of $\hat{H}$ over all antisymmetric N-electron wave functions,

$$E = <\hat{H}> = \min_{\Psi} < \Psi|\hat{H}|\Psi > . \tag{1.13}$$

Defining the electron density as $n(\mathbf{r}) = <\hat{n}(\mathbf{r})>$, this minimization can formally be separated into two steps,

$$E = \min_{n(\mathbf{r})} \left\{ F[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,d\mathbf{r} \right\} \tag{1.14}$$

and

$$F[n] = \min_{\Psi \to n} < \Psi|\hat{T} + \hat{V}_{ee}|\Psi > . \tag{1.15}$$

An equation for the optimal electron density, i.e., the density $n(\mathbf{r})$ which minimizes the total electronic energy, is now obtained by applying the Euler-Lagrange equation to Eq. (1.14), yielding

$$\frac{\delta F}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) = \mu, \tag{1.16}$$

where $\delta F/\delta n(\mathbf{r})$ is a functional derivative and μ is a Lagrange multiplier, corresponding to the constraint

$$\int n(\mathbf{r})\,d\mathbf{r} = N. \qquad (1.17)$$

The Hohenberg-Kohn theorem[8] states that Eq. (1.16) yields the exact ground-state electron density, $n_{GS}(\mathbf{r})$. However, the true density functional $F[n]$ is unknown for most physically interesting systems.

Consider now a fictitious system of noninteracting electrons moving in an external potential $V_{ext}^S(\mathbf{r})$. The Hamiltonian of this system can be written

$$\hat{H}_S = \hat{T} + \int V_{ext}^S(\mathbf{r})\hat{n}(\mathbf{r})\,d\mathbf{r}. \qquad (1.18)$$

The ground-state energy is

$$E_S = \min_{n(\mathbf{r})}\left\{ T_S[n] + \int V_{ext}^S(\mathbf{r})n(\mathbf{r})\,d\mathbf{r} \right\}, \qquad (1.19)$$

where

$$T_S[n] = \min_{\Psi \to n} <\Psi|\hat{T}|\Psi>, \qquad (1.20)$$

leading to the Euler-Lagrange equation

$$\frac{\delta T_S}{\delta n(\mathbf{r})} + V_{ext}^S(\mathbf{r}) = \mu. \qquad (1.21)$$

This relation is equivalent to a set of one-electron Schrödinger equations,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}^S(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \qquad (1.22)$$

which is seen by noting that

$$n(\mathbf{r}) = \sum_i^{occ} |\psi_i(\mathbf{r})|^2, \qquad (1.23)$$

$$T_S = \sum_i^{occ} <\psi_i| -\frac{\hbar^2}{2m}\nabla^2|\psi_i>, \qquad (1.24)$$

where the sums are taken only over occupied states.

Returning to the interacting N-electron system, we write

$$F[n] = T_S[n] + E_{xc}[n] + \frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}d\mathbf{r}'. \qquad (1.25)$$

With this separation of $F[n]$, we note that Eqs. (1.16) and (1.21) can be made equivalent by setting

$$V_{\text{ext}}^{S}(\mathbf{r}) \;=\; V_{\text{ext}}(\mathbf{r}) + e^{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} \qquad (1.26)$$

$$\;=\; V_{\text{ext}}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \qquad (1.27)$$

Thus, it is possible to define one-electron wave functions ψ_i (Kohn-Sham orbitals) that satisfy a Schrödinger equation with a potential $V_{\text{ext}}^{S}(\mathbf{r})$ that consists of an external part, $V_{\text{ext}}(\mathbf{r})$, a Hartree potential, $V_{H}(\mathbf{r})$, and an *exchange-correlation potential*, $V_{\text{xc}}(\mathbf{r})$. From these Kohn-Sham orbitals, $\psi_i(\mathbf{r})$, the ground-state energy of an electronic system is exactly obtained by inserting the electron density $n(\mathbf{r}) = \sum |\psi_i(\mathbf{r})|^{2}$ into the density functional in Eq. (1.14).

The formalism described above is essentially a way of concentrating all non-trivial electronic interactions into one single term, i.e., the exchange-correlation energy functional, $E_{\text{xc}}[n]$. This might not seem to be such a great achievement since $E_{\text{xc}}[n]$ is unknown for most physical systems. However, Fig. 1.1 indicates
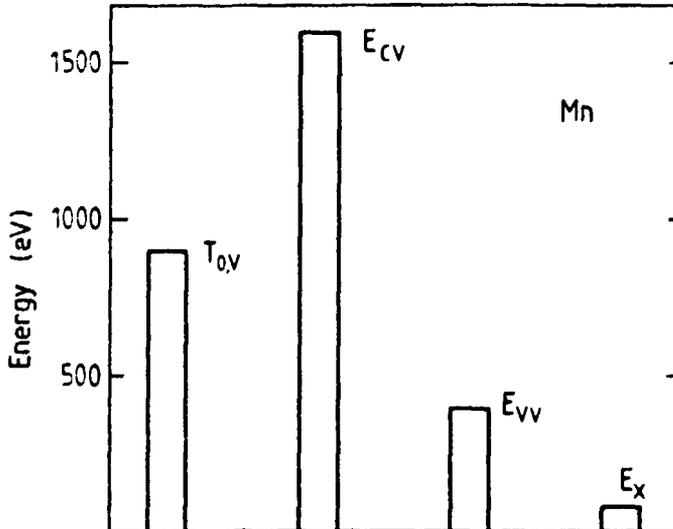
Figure 1.1: Contributions to the total energy of an Mn atom. From Jones and Gunnarsson.[11]

that $E_{\text{xc}}[n]$ typically *is* much smaller in magnitude than the kinetic energy of valence electrons $(T_{0,v})$, the electrostatic energy due to interactions between core and valence electrons (E_{cv}), and the electrostatic energy from interactions between valence electrons (E_{vv}). Since the latter quantities are treated exactly

in the density-functional approach, it is reasonable to believe that an approximate exchange-correlation functional might yield ground-state energies in good agreement with exact results.

Before entering the description of various approximate exchange-correlation functionals, we note a few exact properties of $E_{xc}[n]$. It is useful to define a quantity $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$, through

$$E_{xc}[n] = \frac{e^2}{2} \int \int n(\mathbf{r}) \frac{n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} \, d\mathbf{r}'. \tag{1.28}$$

In this formulation, $E_{xc}[n]$ is conceived as an electrostatic energy between an electron at $\mathbf{r}$ and its *exchange-correlation hole*, $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$. If $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ is divided into separate parts due to exchange and correlation effects, $n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = n_x(\mathbf{r}, \mathbf{r}' - \mathbf{r}) + n_c(\mathbf{r}, \mathbf{r}' - \mathbf{r})$, it can be shown that[3]

$$n_x(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \leq 0, \tag{1.29}$$

$$\int n_x(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \, d\mathbf{r}' = -1, \tag{1.30}$$

$$\int n_c(\mathbf{r}, \mathbf{r}' - \mathbf{r}) \, d\mathbf{r}' = 0. \tag{1.31}$$

For the following discussion of approximate exchange-correlation density functionals, it is useful to note that $E_{xc}[n]$ in Eq. (1.28) only depends on a spherical average of the exchange-correlation hole.[14] This is seen by substituting $\mathbf{R} = \mathbf{r}' - \mathbf{r}$ in Eq. (1.28), yielding

$$E_{xc}[n] = \frac{e^2}{2} \int d\mathbf{r} \, n(\mathbf{r}) \int \frac{dR}{R} \int d\Omega \, n_{xc}(\mathbf{r}, \mathbf{R}). \tag{1.32}$$

1.4 The local density approximation

The exact exchange-correlation density functional, $E_{xc}[n]$, which is defined implicitly by Eq. (1.25), is at the present stage not available for most electron densities, $n(\mathbf{r})$, of physical interest. An important exception is the homogeneous electron gas, where an exact quantum-mechanical treatment is possible. Thus, an accurate function $\varepsilon_{xc}(n)$, describing the exchange-correlation energy of a homogeneous electron gas with density n, can be obtained by fitting analytical functions to results from, e.g., quantum Monte-Carlo calculations.[15]

In the *local density approximation* (LDA), the exchange-correlation energy of an electronic system with varying density, $n(\mathbf{r})$, is approximated by an integral over the energy function of a homogeneous electron gas,

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) \, d\mathbf{r}. \tag{1.33}$$

Various different expressions for $E_{xc}^{LDA}[n]$ exist,[14-20] corresponding to different parametrizations of $\varepsilon_{xc}(n)$.

Strictly, the LDA is valid only for systems with slowly varying electron densities. Thus, it was originally expected to be appropriate for studying, e.g., valence properties of free-electron-like simple metals, while it was thought that atoms, transition metals and surfaces were far beyond the scope of Eq. (1.33). Fortunately, these expectations proved to be wrong. During the last two decades, the LDA and its extension to spin-polarized systems – the local spin-density approximation (LSDA) – have been successfully used for calculations of a variety of electronic properties of atoms, molecules and solids.[11,12]

The success of the local description of exchange-correlation effects is not only theoretically interesting, but is also of fundamental importance for the construction of new improved functionals. The accuracy of the LDA may seem surprising when exchange-correlation holes, $n_{xc}(\mathbf{r}, \mathbf{r'} - \mathbf{r})$, predicted by the LDA are compared with exact results. The upper curves in Fig. 1.2 show the exact and the LDA exchange holes, $n_x(\mathbf{r}, \mathbf{r'} - \mathbf{r})$, plotted in a radial direction from the nucleus, for two different positions ($r=0.13$ and 0.63 a.u.) in the electronic structure surrounding a nitrogen atom. Obviously, the LDA exchange hole is very different from the exact result. However, as shown in Eq. (1.32), the exchange-correlation (exchange) energy depends only on a spherical average of the exchange-correlation (exchange) hole.[14] The spherically averaged exchange holes for the nitrogen atom are shown in the lower curves of Fig. 1.2. The exact and the LDA curves are now strikingly similar, which explains why the LDA gives exchange-correlation energies for light atoms in good agreement with exact results. This example indicates that the success of the LDA in electronic structure calculations is heavily dependent on error cancellations. It has been suggested that the sum rules (1.30) and (1.31) are crucial for such cancellations to take place. Since the LDA is exact for a real physical system (the homogeneous electron gas), it does in fact satisfy the relations (1.29)-(1.31).

1.5   The generalized gradient approximation

The local density exchange-correlation energy expression [Eq. (1.33)] can be regarded as the zero order term in an expansion of $E_{xc}[n]$ to successively higher orders in $n(\mathbf{r})$ and its derivatives. It is then natural to investigate the properties of the exchange-correlation functional that includes the next term in this expansion,

$$E_{xc}^{GEA}[n] = E_{xc}^{LDA}[n] + \int C(n)\frac{(\nabla n)^2}{n^{4/3}}\,d\mathbf{r'}. \tag{1.34}$$
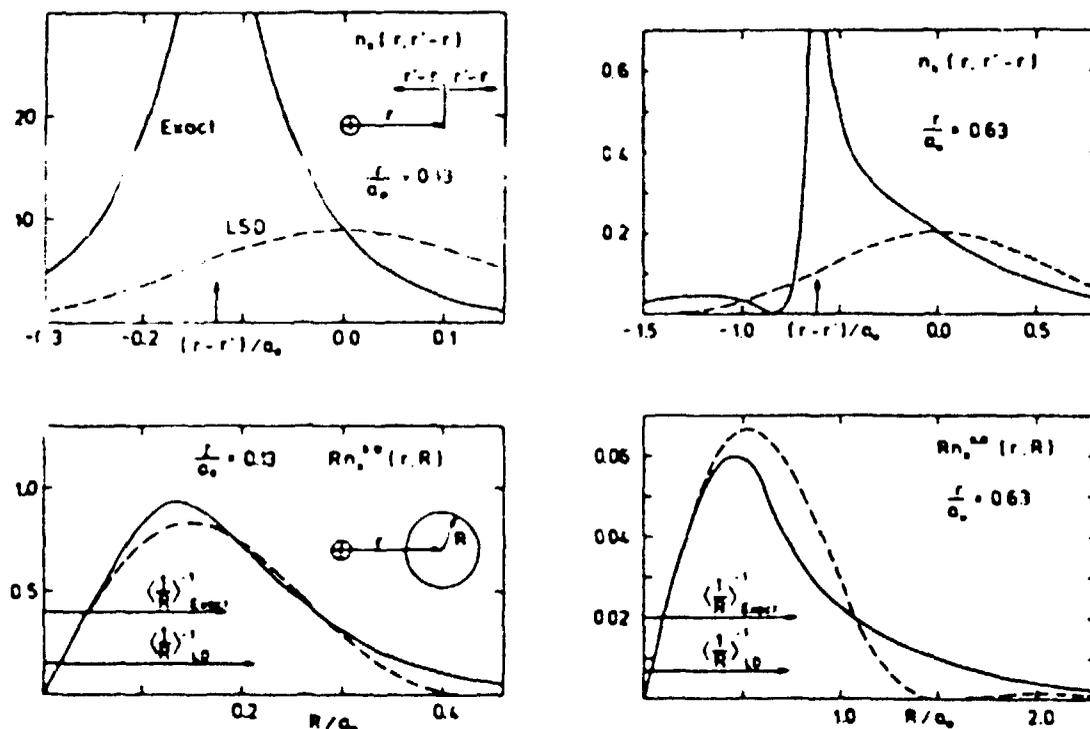
Figure 1.2: Exact (solid line) and LDA (dashed line) exchange hole for a spin-up electron in a nitrogen atom for $r = 0.13$ and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. From Jones and Gunnarsson.[11]

This defines the *gradient expansion approximation* (GEA). The GEA was suggested early by Hohenberg, Kohn and Sham[8,9] as a possible extension of the LDA, and the correct expansion function, $C(n)$, was calculated by Rasolt and Geldart.

The GEA can be shown to improve the short-range behaviour of the LDA exchange correlation hole. However, in most applications, the GEA gives results which are in *worse* agreement with experiment.[22-24] The reason for this failure is probably that the GEA worsens the long-range behaviour of $n_{xc}(r, r' - r)$. In particular, it can be shown that $n_{xc}^{GEA}(r, r' - r)$ violates the properties (1.29)-(1.31) of the exact exchange-correlation hole. This observation is the basis for more recent attempts to improve the LDA.[25-31] Since these new functionals include gradient terms, without being true gradient expansions, they are referred to as *generalized gradient approximations* (GGA).

We here give a brief account of some of the ideas behind the GGA suggested
by Perdew and Wang.[28-31] This functional is presently the most recent GGA,
and some of the basic ideas behind its construction are intuitively easy to un-
derstand.

The GGA of Perdew and Wang[28-31] is constructed so as to include gra-
dient corrections to the exchange-correlation hole while preserving all known
exact features of the LDA. Thus, the negative sign of the exchange hole den-
sity [Eq. (1.29)] and the sum rules (1.30) and (1.31) are enforced through a
real-space cutoff of the GEA exchange-correlation hole. This is illustrated in
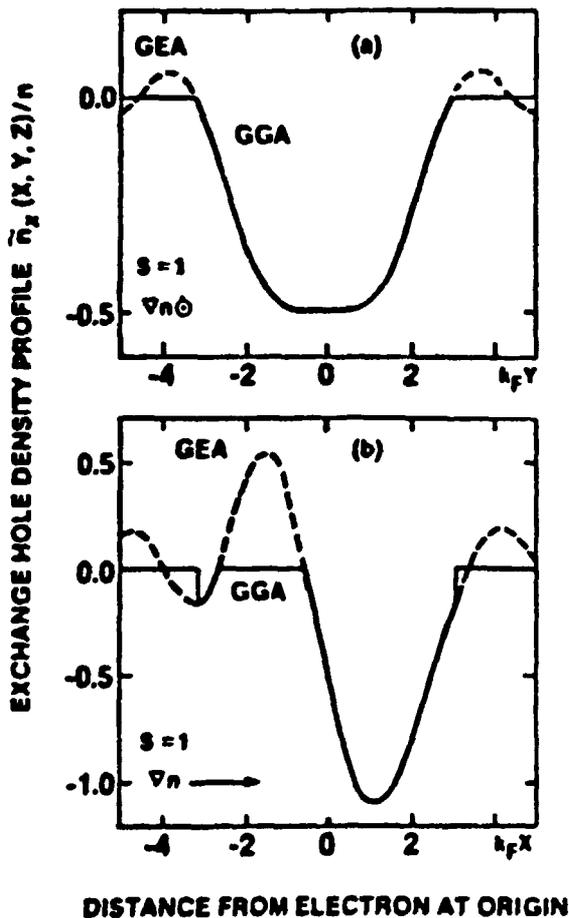
Figure 1.3: Exchange holes in the GEA and the GGA. From Perdew.[22]

Fig. 1.3, which shows the GEA and GGA exchange holes around an electron
at r in directions perpendicular (a) and parallel (b) to an electron density gra-
dient, ∇n. Figure 1.3 clearly shows that the spurious, oscillatory, long-range

behaviour of $n_x^{\mathrm{GEA}}(\mathbf{r}, \mathbf{r}' - \mathbf{r})$ is removed in the GGA.

Apart from obeying Eqs. (1.29)-(1.31), the GGA of Perdew and Wang has been parametrized in order to satisfy other properties of the exact exchange-correlation functional, such as bounds[32] and scaling relations.[33,34] We refer to Refs. 30, 31, 34 for a discussion of these additional features.

Perdew *et al.*[35] have suggested a model which allows for a simple understanding of what type of corrections to LDA results can be expected from the GGA. The GGA exchange-correlation energy can be written

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int n(\mathbf{r})\varepsilon_x(r_S)F_{\mathrm{xc}}(r_S, s)\, d\mathbf{r}. \tag{1.35}$$

Here, the electron density is parametrized by a local Seitz radius, r_S, defined by

$$\frac{4\pi}{3}\left(\frac{r_S}{a_0}\right)^3 = \frac{1}{n}, \tag{1.36}$$

where a_0 is the Bohr radius. The quantity $F_{\mathrm{xc}}(r_S, s)$ is expressed as a function of r_S and of a reduced density gradient, $s = |\nabla n|/2k_F n$, where k_F is a local Fermi wave vector defined through $n = k_F^3/3\pi^2$. It is instructive to compare $F_{\mathrm{xc}}(r_S, s)$ with the local-density part of the exchange-correlation functional, corresponding to $F_{\mathrm{xc}}(r_S, 0)$. Figure 1.4 shows $F_{\mathrm{xc}}(r_S, s)$ for a few electron densities, parametrized by r_S. We note that $F_{\mathrm{xc}}(r_S, s)$ is a monotonously increasing function for most electron densities that occur in atoms and solids ($r_S < 20$ for most metals). Thus, the GGA will energetically favour inhomogeneities in $n(\mathbf{r})$. This effect is consistent with the fact that the GGA yields larger equilibrium distances between atoms in molecules and solids than the LDA. The s-dependence of $F_{\mathrm{xc}}(r_S, s)$ can also be used to qualitatively understand why cohesive energies for solids are lower using the GGA than the LDA, by arguing that atoms are energetically more favoured than solids, since the former have larger variations in valence electron densities.
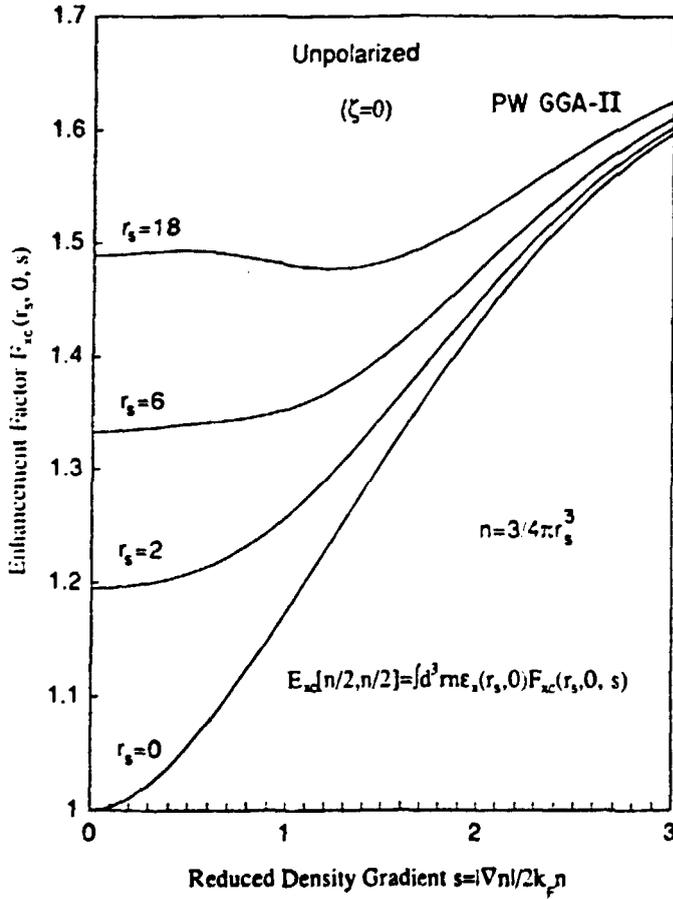
Figure 1.4: Exchange-correlation enhancement function, $F_{xc}(r_S, s)$, versus the reduced density gradient, s. From Perdew *et al.*[35]

Chapter 2

Electronic structures

2.1 Introduction

Electronic states in a periodic crystal can be written as Bloch sums of orbitals centered at atomic sites $\mathbf{R}$,

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{r} - \mathbf{R}). \tag{2.1}$$

The energy band-structure consists of the eigenvalues, $E_j^{\mathbf{k}}$, of the one-electron Schrödinger equation,

$$H\psi_j^{\mathbf{k}}(\mathbf{r}) = E_j^{\mathbf{k}}\psi_j^{\mathbf{k}}(\mathbf{r}), \tag{2.2}$$

where

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}). \tag{2.3}$$

$V(\mathbf{r})$ is here the exact one-electron potential, containing contributions from electron-electron, electron-ion and ion-ion interactions.

One way of solving the Schrödinger equation is to expand the wave functions, $\psi_j^{\mathbf{k}}(\mathbf{r})$, in some basis set, $\{\chi_L^{\mathbf{k}}\}_{L=1}^{L_{max}}$,

$$\psi_j^{\mathbf{k}}(\mathbf{r}) = \sum_{L=1}^{L_{max}} A_{Lj}^{\mathbf{k}} \chi_L^{\mathbf{k}}(\mathbf{r}). \tag{2.4}$$

By applying the Rayleigh-Ritz variational principle, Eq. (2.2) can be transformed into a system of linear equations for the expansion coefficients, $A_{Lj}^{\mathbf{k}}$,

$$\sum_{L} \left(H_{L'L}^{\mathbf{k}} - E_j^{\mathbf{k}} O_{L'L}^{\mathbf{k}} \right) A_{Lj}^{\mathbf{k}} = 0, \tag{2.5}$$

13

where $H_{L'L}^{\mathbf{k}}$ and $O_{L'L}^{\mathbf{k}}$ are the Hamiltonian and overlap matrices, respectively, defined through

$$H_{L'L}^{\mathbf{k}} \; = \; < \chi_{L'}^{\mathbf{k}} |H| \chi_L^{\mathbf{k}} >, \qquad (2.6)$$

$$O_{L'L}^{\mathbf{k}} \; = \; < \chi_{L'}^{\mathbf{k}} | \chi_L^{\mathbf{k}} > . \qquad (2.7)$$

It is important to note that, in the formalism leading to a linear system of equations (2.5), all $\psi_j^{\mathbf{k}}$ are expanded in the same, energy-independent basis functions, $\chi_L^{\mathbf{k}}$. The difficulty of the diagonalization problem [Eq. (2.5)] heavily depends on the choice of $\chi_L^{\mathbf{k}}$, i.e., on the number of terms needed for a satisfactory convergence of the wave function expansion in Eq. (2.4).

2.2   The LMTO method

Several methods for band-structure calculations on solids lead to a linear diagonalization problem [Eq. (2.5)]. At the present stage, the linear-augmented-plane-waves (LAPW)[36-39] and the linear-muffin-tin-orbitals (LMTO)[36,40,41] approaches are the most commonly used. We here restrict ourselves to a brief account of some basic concepts of the LMTO method, while more complete presentations are found in the original article by Andersen[36] and in the book by Skriver.[41] For simplicity, we describe the LMTO approach in the muffin-tin (MT) potential approximation, i.e., when the crystal potential, $V(\mathbf{r})$, is approximated by a spherically symmetric part in each so-called MT sphere surrounding an atom ($r \leq S$), and by a constant in the interstitial region. This potential shape is schematically drawn in Fig. 2.1. The MT potential approximation, which often is used together with so-called combined correction terms,[41] is adequate for calculations on close packed structures and for describing the energetics of non-symmetry breaking atomic displacements. However, it has proven insufficient for total-energy calculations on sheared crystals or on lattices containing vacancies. We will also restrict our account to the non-relativistic case, while it is common practice in band-structure calculations to treat core electrons fully relativistically and valence electrons in the so-called semirelativistic approximation, i.e., when spin-orbit coupling is neglected.[42]

It should be noted that several authors[43-48] have recently suggested LMTO approaches that include angular dependencies in the crystal potential. Results from these calculations are very promising and the computer-time requirement is only moderately increased compared with calculations using MT potentials.

Assuming an angular-independent potential, $V(r)$, inside the MT sphere surrounding each atom, we write the wave function for an electronic state at a
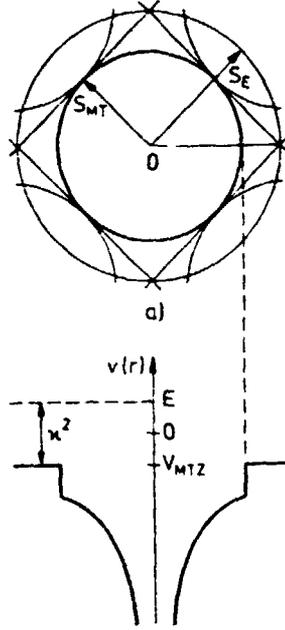
Figure 2.1: The muffin-tin potential. From Skriver.[41]

certain energy, E, as

$$\phi(E, \mathbf{r}) = \sum_{lm} \phi_\ell(E, r) i^\ell Y_{\ell m}(\theta, \varphi), \qquad (2.8)$$

where $Y_{\ell m}(\theta, \varphi)$ are spherical harmonics. $\phi_\ell(E, r)$ is the solution to the radial Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{e^2 \ell(\ell + 1)}{r^2} + V(r) - E \right] r \phi_\ell(E, r) = 0. \qquad (2.9)$$

Outside the MT-sphere ($r > S$), we choose $\phi_\ell(r) \sim (S/r)^{\ell+1}$, which is the bounded solution of Laplaces equation. This tail wave function is exact in the limit of zero kinetic energy, κ. Thus, it is valid for small $E - V_{\mathrm{MTZ}}$, where V_{MTZ} is the zero level of the muffin-tin potential (cf. Fig. 2.1).

Obviously, the solution, $\phi(E, r)$, of Eq. (2.9) is energy dependent. In the previous section we showed that the band structure problem [Eq. (2.2)] can be written as a linear eigenvalue problem if the total wave function is expanded in an energy-independent basis set. We therefore consider the radial wave function at some arbitrary but fixed energy, E_ν,

$$\phi_{\nu\ell}(r) = \phi_\ell(E_\nu, r). \qquad (2.10)$$

Further, we define the energy derivative of $\phi_\ell(E, r)$ at E_ν,

$$\dot{\phi}_{\nu\ell}(r) = \left. \frac{\partial \phi_\ell(E, r)}{\partial E} \right|_{E_\nu}. \tag{2.11}$$

The exact radial wave function can now be expanded in $\phi_{\nu\ell}$ and $\dot{\phi}_{\nu\ell}$ to first order in $(E - E_\nu)$,

$$\phi_\ell(E, r) = \phi_{\nu\ell}(r) + (E - E_\nu)\dot{\phi}_{\nu\ell}(r) + \mathcal{O}[(E - E_\nu)^2] \tag{2.12}$$

The matching of the solutions inside and outside the MT spheres implies continuity in the logarithmic derivative of $\phi_{\nu\ell}(r)$ at $r = S$. It is useful to define

$$D_{\nu\ell} = S \frac{\phi'_{\nu\ell}(S)}{\phi_{\nu\ell}(S)}, \tag{2.13}$$

where the prime $(')$ refers to derivation with respect to r. A linear combination of $\phi_{\nu\ell}$ and $\dot{\phi}_{\nu\ell}$, with arbitrary logarithmic derivative at $r = S$, can be written,

$$\Phi_{\nu\ell}(D, r) = \phi_{\nu\ell}(r) + \omega_{\nu\ell}(D)\dot{\phi}_{\nu\ell}(r). \tag{2.14}$$

The total *muffin-tin-orbital* (MTO) can now be defined as

$$\Phi_{\nu\ell m}(-\ell - 1, \mathbf{r}) = i^\ell Y_{\ell m}(\theta, \varphi) \begin{cases} \Phi_{\nu\ell}(-\ell - 1, r) & r \leq S, \\ A(S/r)^{\ell+1} & r > S, \end{cases} \tag{2.15}$$

where A is a constant. Here, $D = -\ell - 1$ is due to the matching of logarithmic derivatives at $r = S$.

We now return to the Bloch states in Eqs. (2.1) and (2.4). Using the muffin-tin-orbitals defined in Eq. (2.15), the total wave function, $\chi_L^{\mathbf{k}}(\mathbf{r})$, around an atom at $\mathbf{r} = \mathbf{R}$ has contributions from the MTO centered at $\mathbf{R}$ and from the tails of all MTO's at other lattice sites in the crystal. It can be shown[41] that this tail sum may be written as a one-center expansion of MTO's, centered at $\mathbf{R}$. This expansion is convergent inside the MT sphere surrounding $\mathbf{R}$. For an atom at the origin, we write

$$\chi_L^{\mathbf{k}}(\mathbf{r}) = \Phi_{\nu L}(-\ell - 1, \mathbf{r}) - \sum_{L'} \frac{\Phi_{\nu L'}(\ell', \mathbf{r})}{2(2\ell' + 1)} \frac{\phi_\ell(-\ell - 1)}{\phi_{\ell'}(\ell')} S_{L'L}^{\mathbf{k}}, \tag{2.16}$$

where the notations $\phi_\ell(\ell) = \phi_\ell(\ell, S)$ and $L = \ell m$ have been used. Further, we have defined *structure constants*

$$S_{L'L}^{\mathbf{k}} = g_{L'L} \sum_{\mathbf{R} \neq 0} e^{i\mathbf{k}\cdot\mathbf{R}} \left(\frac{S}{R}\right)^{\ell''+1} [\sqrt{4\pi} i^{\ell''} Y_{\ell''m''}(\hat{R})]^*, \tag{2.17}$$

where $\ell'' = \ell' + \ell$, $m'' = m' - m$, and $g_{L'L}$ are so-called Gaunt coefficients.[41] It should be noted that, since $S^{\mathbf{k}}_{L'L}$ are independent of Φ_L, they need to be calculated only once for each crystal structure.

In summary, the LMTO method is an elaborate scheme for choosing an energy-independent basis set for electronic wave functions in solids. Since these basis functions are equal to the true solutions of the Schrödinger equation to low order in the energy differences $(E - E_\nu)$ and $(E - V_{\mathrm{MTZ}})$, they often give a rapidly convergent series expansion of the exact wave function [Eq. (2.4)]. This reduces the size of the diagonalization problem [Eq. (2.5)], and it increases the speed of computer calculations.

Chapter 3

Band-structure results

3.1 Introduction

Electronic structure calculations on solids represent a large and rapidly growing research field. In the following sections, we give a few examples of questions which have attracted interest during recent years and which also are related to the topics treated in this thesis. Further, we comment on some problems which still remain to be solved.

3.2 Band structures and bonding theory

One of the most important roles of electronic band-structure calculations[49] is to simplify the interpretations of experimental studies of electronic energy spectra. The possibility of a direct identification of the atomic origin and the partial ℓ-character of electron bands has been of great importance for a better theoretical understanding of how physical properties vary in different classes of materials. For example, qualitative arguments based on the electronic energy spectrum have explained how the ground-state crystal structure of the elements changes in the Periodic Table.[50-53] Further, the ground-state properties of simple compounds, e.g., the NaCl-type structure borides,[54] carbides,[55-59] nitrides[55-59] (Papers 1-3) and oxides[55] of the transition metals, have been discussed in terms of the character of the occupied part of the electronic density of states. These works have shown that the importance of different types of bonds (e.g., metal-nonmetal or metal-metal bonds) may differ along a series of compounds, and theories which generalize the chemists' traditional view of bonding and antibonding orbitals have been suggested[60-62] (Paper 4).

The character of electronic states is particularly important for many materials of current interest, such as high-T_C superconductors and organic crystalline molecules. The complexity of the crystal structure of these materials is a challenge to theoretical electronic structure determinations and it reveals the need for a development of improved schemes that can handle large unit cells (> 20 atoms).

There is ample evidence that a density-functional approach in the local-density approximation is appropriate in most cases for calculations of electronic energy spectra. However, there are a few cases where band-structure calculations, relying on the local-density approximation, give an entirely incorrect electronic ground-state energy spectrum. For example, certain insulating oxides of the $3d$-transition metals (e.g., FeO, CoO and CuO) are predicted to be metallic in band-structure calculations using the LDA,[63] while other oxides (e.g., MnO and NiO) get band-gaps that are much smaller than experimental values. It has been shown[64] that functionals including gradient corrections[28-31] do not give the correct energy spectrum, while calculations including explicit self-interaction corrections (SIC) have been reported[65] to yield ground-state electronic configurations in very good agreement with experiment.

3.3   Cohesive energies and enthalpy differences

Band-structure calculations can be used to predict various ground-state properties of solids such as equilibrium lattice parameters, bulk moduli and cohesive energies. Since these quantities are derived from differences in calculated total electronic energies, they rely heavily on the accuracy of the theoretical model. Transition metals and transition metal compounds are important for many applications. Unfortunately, the discrepancy between calculated ground-state properties and experimental results is large for these materials. Typically,[66] *ab initio* calculations yield lattice parameters that are too small by up to 5%, bulk moduli that are overestimated by up to 20%, and cohesive energies per atom that are approximately 1 eV larger than experimental results.

After the early *ab initio* calculations on $3d$- and $4d$-transition metals by Moruzzi, Janak and Williams,[66] there has been no major breakthrough in improving the accuracy of theoretical results. However, there have been several works which have analysed the origin of the errors in *ab initio* calculations. For example, Watson and co-workers[67,68] showed that a general potential treatment gives a significant further increase in cohesive energies, i.e., a worse agreement with experiment. Apparently, the major part of the errors in theoretical results for elements and simple compounds may be attributed to the approximate treatment of electronic exchange-correlation interactions in the LDA. This is why there has recently been much interest in the new GGA functionals[28-31]

and their application in band structure calculations on transition metals. The results from these studies indicate an improvement in calculated lattice parameters, bulk moduli and cohesive energies for simple metals and $3d$-transition metals[35,64,69-78] (Papers 8,9). For elements in the $4d$- and $5d$-series, an overcompensation of errors has been observed,[70,72,78] (Paper 8) but the reason for this effect is still unclear. It has recently been reported that the GGA overestimates the magnetic moments of certain transition-metals (e.g., bcc Cr[79,80] and Invar alloys[73,80]). However, the comparison with experimental results is difficult for these materials. For example, the ground-state magnetic structure of Cr can be described by a spin-wave with a periodicity that is incommensurate with the crystal lattice, while *ab initio* results[79,80] refer to an antiferromagnetic structure with two atoms per unit cell.

An attractive feature of theoretical total energy determinations is that they allow for an investigation of metastable states. By "metastable", we refer to compositions or structures of compounds and elements that do not represent the lowest free energy at thermal equilibrium. These phases may still influence the properties of real materials, since many processing techniques (casting, annealing, etc) do not yield solids at thermal equilibrium. Furthermore, the relative stability of stable and metastable phases is important for understanding and predicting phase diagrams. The use of *ab initio* results for determining enthalpies of formation has been limited by the large absolute errors in theoretical results. However, it has been suggested[57,58] (Papers 2,3) that quantitative predictions can still be successfully obtained from total energy results by comparing trends in theoretical and experimental values.

An interesting application of theoretical calculations is to determine the enthalpy differences between various crystal structures of the elements (e.g., bcc, fcc and hcp). These quantities are of interest in metallurgy since they determine the low-temperature part of the equilibrium phase diagram. Several independent calculations of fcc–bcc and fcc–hcp enthalpy differences [$\Delta^0 H$(fcc–bcc) and $\Delta^0 H$(fcc–hcp)] have been performed over the years.[52,53,67,81,82] Barring a few cases (e.g., Fe[83-87]), band-structure calculations relying on the local-density approximation yield the correct ground-state crystal structure. However, the magnitude of $\Delta^0 H$(fcc–bcc) and $\Delta^0 H$(fcc–hcp) has been very difficult to reconcile with experimental results.[88-93] Recent results from MT-potential calculations on the $4d$-transition metals[94] show that gradient corrections to the exchange-correlation functional reduce the discrepancy between theory and experiment (cf. Fig. 3.1). These results are interesting, especially since gradient corrections from angular variations in the crystal potential may give further improvements.

The fact that the LDA predicts a nonmagnetic fcc phase of iron to be more stable than the experimentally observed ferromagnetic bcc phase has attracted a considerable amount of interest during recent years.[83-87] It is now well estab-
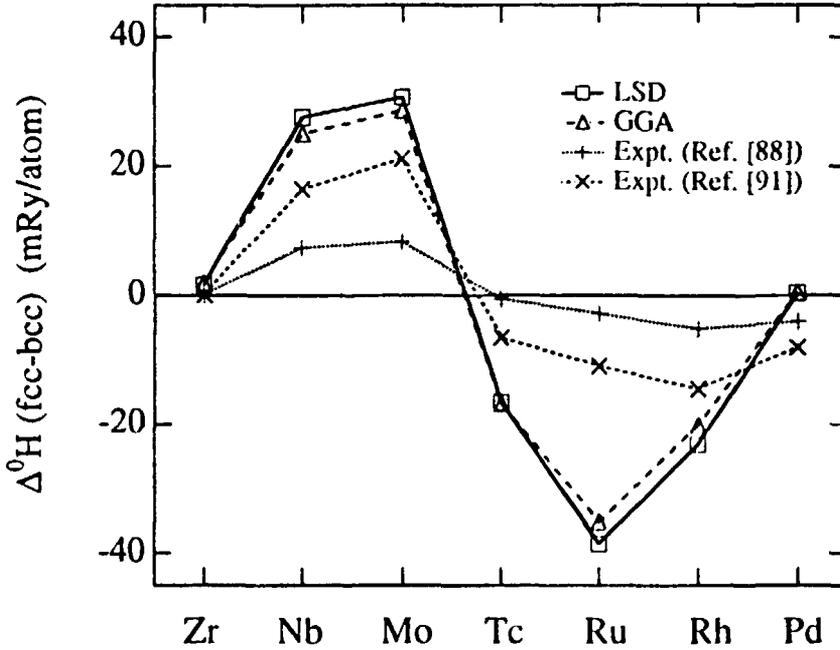
Figure 3.1: $\Delta^0 H$(fcc–bcc) from LMTO calculations[94] using the LDA and the GGA. $\Delta^0 H$(fcc–bcc) values from experimental information are from Refs. 88, 91.

lished[87] that the incorrect enthalpy difference is an artifact of the incomplete treatment of exchange-correlation effects in the LDA. An important success of the new GGA exchange-correlation functional by Perdew and Wang[28–31] is that it gives the correct ground-state for iron.[64,71–78]

3.4   Elasticity and vibrations

The determination of elastic constants is straightforward in *ab initio* calculations. By applying a strain to a periodic lattice, a force constant is obtained from the shift in total electronic energy. Bulk moduli are particularly simple to calculate, since they are derived from the energy shift due to a hydrostatic compression (or expansion) of a crystal. For cubic crystals, this deformation does not influence the lattice symmetry, and the total energy is determined for an unchanged number of atoms per unit cell. For other elastic constants, the corresponding strain tensors[95–98] will lower the lattice symmetry and thus increase the computational effort. Moreover, such calculations are sensitive
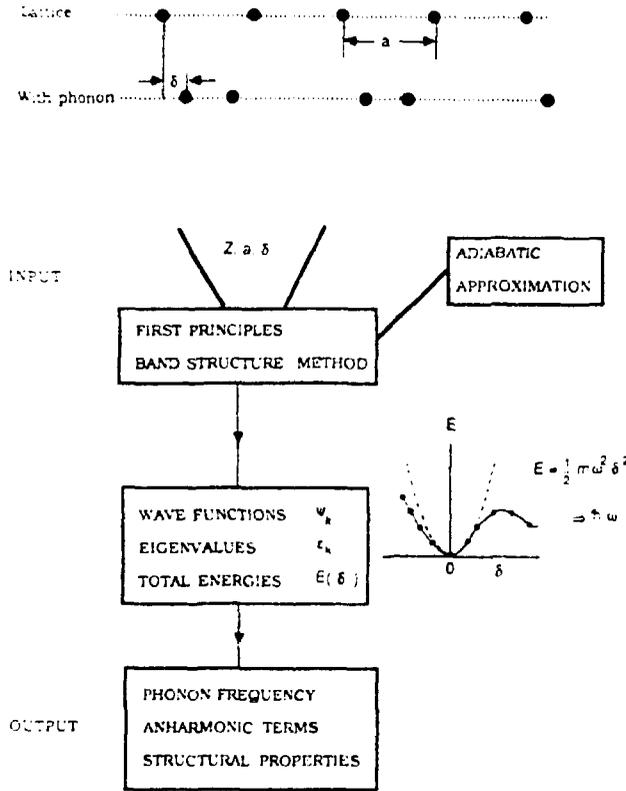
Figure 3.2: Schematic description of the frozen phonon approach. From Ho and Harmon.[102]

to non-spherical terms in the crystal potential. This explains why, e.g., shear moduli are poorly predicted using the muffin-tin potential approximation.[99,100]

The frequencies of long-wavelength lattice vibrations are directly related to the elastic constants. Hence, the $k \rightarrow 0$ limit of the phonon spectrum can be analysed using *ab initio* calculations on compressed or sheared lattices. A similar approach can be used[101,102] to determine frequencies of other phonon modes. This is achieved by "freezing" the crystal in a structure that corresponds to the amplitude of a certain phonon mode and by calculating the change in total electronic energy due to this lattice deformation. This approach relies on the separation of electronic and ionic degrees of freedom, i.e., the Born-Oppenheimer approximation (cf. Fig. 3.2). The "frozen phonon" approach is limited by the relatively small number of atoms per unit cell that can presently be handled with sufficient accuracy in *ab initio* calculations. It can,

therefore, not be used to study vibrational modes with long wavelengths. An attractive feature of frozen-phonon calculations is that they give simultaneous information on total energies and electronic charge densities. This has been successfully used to analyse experimentally observed anomalies in the phonon spectra of, e.g., Zr,[103-105] Nb[103,104] and Mo.[106-108]

Many physical properties of solids are not sensitive to details in the phonon spectrum, but only to certain characteristic phonon frequencies. It is particularly useful to define *frequency moments*[109] through

$$\omega^n(n) = \frac{\int \omega^n F(\omega)d\omega}{\int F(\omega)d\omega},\qquad(3.1)$$

when $n > -3$ and with ω^n replaced by $\ln\omega$ to define $\omega(0)$. For example, the temperature variations of the vibrational energy and entropy are, to leading order, determined by $\omega(2)$ and $\omega(0)$, respectively, at high temperatures. It is interesting to search for simplified theoretical schemes that can be used to predict characteristic phonon frequencies. A widely used approach[110,111] is to fit a Debye model phonon spectrum to bulk moduli from *ab initio* calculations. Various thermal properties, such as vibrational entropies and energies, are then described within this approximation. However, the Debye model is not accurate enough for most purposes. Moreover, an analysis based entirely on calculated bulk moduli is often unsatisfactory, since the elastic limit of the phonon spectrum is dominated by shear modes.[112]

A different approach, which can be used to determine the frequencies of more general vibrational modes, has recently been presented[113] (Paper 10). It is similar to the frozen-phonon method, since it relies on a total energy calculation on a disordered supercell. The atomic displacements within the supercell are stochastically generated according to independent Gaussian probability distributions. In the limit of harmonic lattice vibrations, it can be shown that the energy associated with this lattice distorsion is directly related to the second moment, $\omega(2)$, of the phonon density-of-states. A relatively large number of atoms per unit cell (> 50) is needed to reduce the effects of periodicity between the supercells. However, by applying an averaging procedure to the LMTO method, this large cell does not reduce the efficiency of the self-consistent-field calculations, compared with a band-structure calculation on an undistorted lattice.

3.5 Magnetic phase transitions

Phase transitions in itinerant magnetic systems is a field where many fundamental questions still remain. Two problems of particular importance concern

the character of pressure-induced transitions at fixed temperature, and the microscopic nature of magnetic excitations above the Curie (Néel) temperature of ferromagnetic (antiferromagnetic) materials. While *ab initio* band structure calculations have been widely used to treat the first of these problems, there is as yet no method available that allows for a complete analysis of temperature effects in magnetic systems. However, a combined use of empirical information and theoretical calculations may help to understand the nature of magnetic excitations.

Most elements in the Periodic Table have local magnetic moments at sufficiently large lattice spacings. This is easily understood by noting that expanded crystals will tend to the atomic state where Hund's rule applies. The lattice spacings where this hypothetical magnetic state exists cannot be experimentally accessed for most elements. However, magneto-volume properties can be successfully analysed in *ab initio* calculations, and Moruzzi and Marcus[114] have shown how the approach towards atomic magnetic moments occurs in the $3d$-transition metals. Electronic structure calculations can also be used to study metastable states, i.e., magnetic states that do not yield the lowest energy at a certain lattice parameter. This type of analysis is often carried out using the so-called fixed-spin-moment (FSM) procedure,[115] which is a technique where the lattice parameter (a_0) and the local magnetic moment (M) are fixed separately. Thus, the entire $E(M, a_0)$ dependence can be determined. The FSM approach has been used to study ferromagnetic and antiferromagnetic states and phase transitions for several $3d$- and $4d$-transition metals in different structures[76,116−121] (Paper 9). An interesting result from these calculations is that V(bcc), Fe(fcc), Co(fcc) and Ni(fcc) are predicted to have four different types of magnetic phase transitions at increasing volume[116] (Fig. 3.3). It is noteworthy that LDA calculations on Fe(fcc) yield two different ferromagnetic phases, corresponding to a low-spin (LS) and a high-spin (HS) state, respectively.

Pressure-induced magnetic phase transitions is a field where the predictive power of theoretical calculations is great and where experimental data is still scarce or completely lacking. Unfortunately, this also means that the validity of theoretical results is difficult to assess. One way of estimating the accuracy of a local-density description of exchange-correlation effects is to compare with results obtained using other functionals. Such tests have been carried out in only a few cases[75,76,79] (Paper 9). The results to date indicate that the relative stability of different magnetic states can be significantly changed by using different exchange-correlation functionals. Thus, there is reason to treat theoretical predictions for metastable magnetic states and magnetic phase transitions with great care.

Temperature-induced magnetic excitations in solids can still not be accounted for with pure *ab initio* methods. Since experimental information on these excitations often is indirect and difficult to interpret, there is no com-
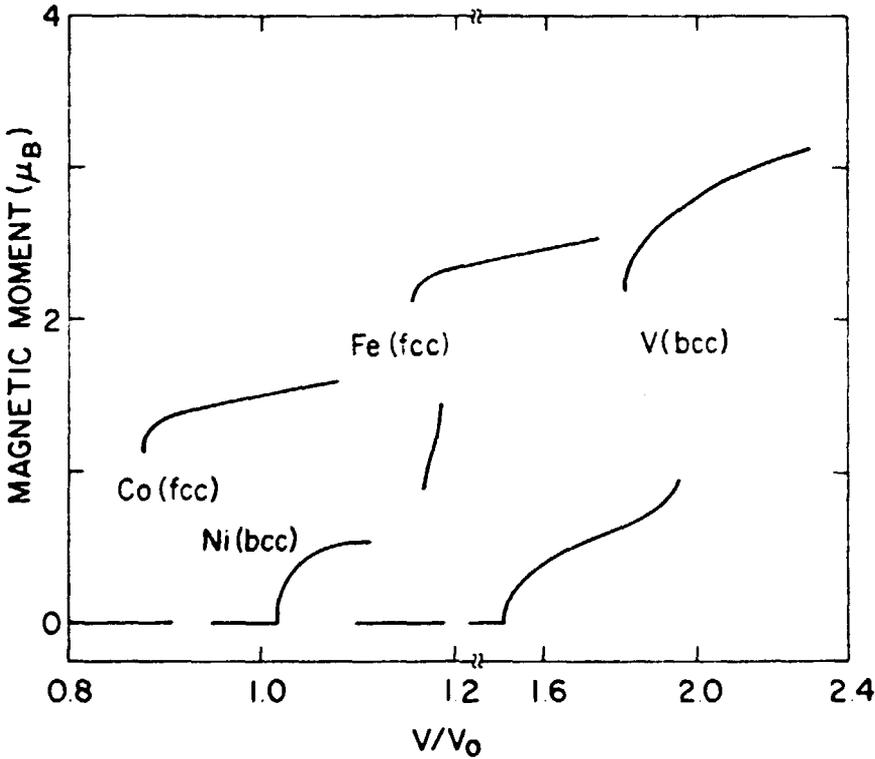
Figure 3.3: Magnetization versus lattice parameter for V(bcc), Fe(fcc), Co(fcc) and Ni(fcc). From Moruzzi.[116]

plete understanding of the microscopic character of magnetic excitations above the Curie (Néel) temperature in itinerant magnetic systems. Although electronic structure calculations alone cannot predict the size of thermally excited magnetic fluctuations in the paramagnetic regime, they can be used as a complement to experimental information, e.g., from calorimetric or neutron scattering experiments. This approach has recently[122] (Paper 11) been applied to paramagnetic chromium. The existence of entropy contributions which do not originate in lattice vibrations or electronic excitations, suggests that Cr has local magnetic moments at temperatures well above the Néel temperature.

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Comments on the papers

Transition-metal carbides and nitrides (papers 1-7)

The first three papers in this series contain results from extensive band-structure calculations and from detailed analyses of experimental information on all $3d$-, $4d$- and $5d$-transition metal carbides and nitrides in the NaCl-type structure. The information on these 48 compounds gives a unique possibility for assessing the accuracy of theoretical results and of the models that are used to extract experimental information on metastable phases. Moreover, it provides a firm ground for studies of trends in chemical bonding in metal-nonmetal compounds (Paper 4). These trends are observed (Paper 4), not only for carbides and nitrides with the NaCl-type structure, but also for compounds with more complex crystal structures (Paper 5). The character of the electronic energy spectrum is important for a qualitative insight into physical phenomena related to bonding strengths. In this thesis, we use such arguments to discuss vacancy formation energies (Paper 6) and surface reconstructions (Paper 7).

Applications of the GGA (papers 8-9)

There is a great need for improved exchange-correlation functionals in electronic structure calculations. Many important applications of theoretical calculations are still impossible because of large errors. There is reason to believe that the generalized gradient approximation (GGA) could provide such an improvement. However, our results on transition metal elements give a scattered picture of the agreement between theoretical and experimental results. In some cases, the GGA gives a significantly better correspondence between theory and experiment (nonmagnetic $3d$-transition metals), while the results for other elements ($5d$-transition metals) are less favourable. We believe that it is too early to draw any certain conclusions from these tests, since the effects of other

approximations that are inherent in the theoretical approach have not yet been properly investigated.

Electronic structures of disordered crystals (paper 10)

The influence of structural disorder on the electronic properties of materials is of fundamental importance to many fields of solid state physics. The most obvious reason for broken periodicity in a crystal is lattice vibrations. Molecular dynamics simulations, based on a quantum mechanical description of electronic interactions (e.g. Car-Parinello methods), will probably be applied to real materials in the future. However, this will require better computational methods, as well as greatly improved computer performances. We believe that there is a need for simple, approximate methods for electronic structure calculations on disordered crystals. We suggest an approach which contains several important approximations but which is extremely efficient for numerical calculations. This approach is used to calculate the structural dependence of the Debye temperatures of the $4d$-transition metals. Good agreement with experiment is obtained for those structures that can be experimentally observed.

Magnetic fluctuations in chromium (paper 11)

The microscopic nature of the paramagnetic state in itinerant ferromagnetic and antiferromagnetic materials is still unclear. We suggest that information on magnetic excitations at high temperatures can be obtained by studying different contributions to the total entropy. This quantity is often accurately known up to melting temperatures from calorimetric measurements. We note that the total entropy for *nonmagnetic* materials approximately equals a sum of a vibrational part and a Sommerfeld-type electronic contribution. Thus, we ascribe an observed excess entropy for bcc Cr at high temperatures to fluctuating local magnetic moments.