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*(H. Winter)*

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*(M. Ohno)*

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*(G. Stefani, R. Gotter, A. Ruocco, F. Offi, F. Da Pieve, A. Verdin, A. Liscio, S. Iacobucci, Hua Yao, and R. Bartynski)*

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Preface

The understanding of the behavior of interacting many-body systems is a goal with a long history dating back to the beginning of modern physics. The interest in this topic is not only due to the intellectual challenge in describing the complex and the fascinating facets of the many-body dynamics. It is also established by now that various important material properties are driven by the correlated behavior of the system’s constituents, as documented by a variety of examples in this book.

The rapid increase in computational resources has triggered an intensive research on the interlink between many-body idealized models and ab-initio single particle approaches. The aim of these theoretical efforts is the development of a realistic theoretical framework capable of capturing many-body effects in electronic materials. This book contains a snapshot on the current status of some of the developments in this direction, namely the implementation of the dynamical mean-field theory and the so-called GW method as well as the calculations based on many-body perturbation theory and the embedded-cluster approach.

On the other hand, in recent years there has been a major advance in the experimental techniques that are capable of imaging the various manifestations of electronic correlation. The most notable progress in this direction is the realization of the coincidence detection of many particles. These experiments allow a detailed insight into the various aspects of the correlated behavior of electronic matter. An overview of the most recent experimental developments is provided by several contributions in this book. A particular emphasis is put on presenting and comparing some of the most prominent techniques presently feasible, namely electron-electron coincidence experiments, electron-ion coincidence techniques, the simultaneous electron-photon detection and photoelectron-Auger electron coincidence spectroscopy.

One of the prime aims of the present book is to highlight the ubiquitous nature of electronic correlations and to stimulate cross fertilization between the various research fields. Therefore, examples are included from atomic, molecular, cluster, surface and solid state physics.

Another aspect which we regard vital for further advances is the close connection between the experimental and the theoretical efforts. Many examples in this book document how theory and experiment can guide each other for finding the appropriate answers and for pointing out to shortcomings and future directions.

The book is based on invited contributions to the conference Coincidence Studies of Surfaces, Thin Films and Nanostructures which took place in September, 2003, at the Ringberg Castle in Germany. We acknowledge with thanks the generous support of the Max-Planck-Institut für Mikrostrukturphysik in Halle and the competent help of H. Schwabe and D. Röder in organizing the workshop.

J. Berakdar and J. Kirschner

Halle, 2004
List of Contributors

- **Oleg Mihailovich Artamonov**, Ch. 6
  Research Institute of Physics, St. Petersburg University, Uljanovskaja 1, Petrodvoretz, 198904 St. Petersburg, Russia

- **Ferdi Aryasetiawan**, Ch. 1, 7
  Research Institute for Computational Sciences, AIST Tsukuba Central 2, Umezono 1-1-1 Tsukuba, Ibaraki 305-8568 Japan
e-mail: f-aryasetiawan@aist.go.jp

- **Robert Bartynski**, Ch. 13, 14
  Department of Physics and Astronomy and Laboratory of Surface Modification, Rutgers University, 136 Frelinghuysen Road, 08855 Piscataway, New Jersey USA
e-mail: bart@physics.rutgers.ed

- **Friedhelm Bell**, Ch. 8
  University of Munich, Am Coulombwall 1, 85748 Garching Germany
e-mail: friedhelm.bell@bnw4u.de

- **Jamal Berakdar**, Ch. 3, 5
  Max-Planck Institut für Mikrostrukturphysik Weinberg 2, 06120 Halle Germany
e-mail: jber@mpi-halle.mpg.de

- **Silke Biermann**, Ch. 1
  Centre de Physique Theorique (CPHT) Ecole Polytechnique 91128 Palaiseau Cedex France
e-mail: Silke.Biermann@cpht.polytechnique.fr

- **Joachim Burgdörfer**, Ch. 10
  Institute for Theoretical Physics Vienna University of Technology Wiedner Hauptstraße 8–10 (E136) 1040 Vienna Austria
e-mail: burg@concord.itp.tuwien.ac.at

- **Cameron Bowles**, Ch. 7
  Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200 Australia

- **C. Creagh**, Ch. 15
  Murdoch University 2-35 Physical Sciences Murdoch Australia
e-mail: thurgate@central.murdoch.edu.au
List of Contributors

• Michal Dallos, Ch. 10
  Institute for Theoretical Chemistry and Structural Biology
  University of Vienna
  Währinger Straße 17/403
  A-1090 Vienna
  Austria
  e-mail: michal.dallos@univie.ac.at

• Fabiana Da Pieve, Ch. 14
  Department of Physics and Unità INFM
  University of Rome, Roma Tre
  Via della Vasca Navale 84
  I-00146 Rome
  Italy
  e-mail: dapieve@fis.uniroma3.it

• Roland Feder, Ch. 9
  Theoretische Festkörperphysik
  Universität Duisburg-Essen,
  D-47048 Duisburg
  Germany
  e-mail: feder3@dagobert.uni-duisburg.de

• Natasha Fominykh, Ch. 3
  Max-Planck Institut für Mikrostrukturphysik
  Weinberg 2,
  06120 Halle
  Germany
  e-mail: fom@mpi-halle.de

• Antoine Georges, Ch. 1
  Laboratoire de Physique Theorique de l’Ecole Normale Superieure
  24, rue Lhomond
  75231 Paris Cedex 05
  France
  e-mail: georges@lpt.ens.fr

• H. Gollisch, Ch. 9
  Theoretische Festkörperphysik
  Universität Duisburg-Essen,
  D-47048 Duisburg
  Germany

• Roberto Gotter, Ch. 14
  National Laboratory TASC-INFM
  Area Science Park
  SS 14 Km 163.5
  I-34012 Basovizza, Trieste
  Italy
  e-mail: gotter@tasc.infm.it

• Steven L. Hulbert, Ch. 13
  National Synchrotron Light Source
  Brookhaven National Laboratory
  Upton, New York 11973
  USA
  e-mail: Hulbert@bnl.gov

• Kouji Isari, Ch. 16
  Research Center for Nanodevices and Systems,
  Hiroshima University,
  1-4-2 Kagamiyama, Higashi-Hiroshima 739-8527
  Japan
  e-mail: isari@sxsys.hiroshima-u.ac.jp

• Stefano Iacobucci, Ch. 14
  IMIP-CNR Area della Ricerca di Roma
  via Salaria Km 29.3
  Montelibretti, Rome
  Italy
  e-mail: iacobucci@fis.uniroma3.it

• Z.-T. Jiang, Ch. 15
  Murdoch University
  Perth, Western Australia

• Anatoli S. Kheifets, Ch. 7
  Atomic and Molecular Physics Laboratories,
  Research School of Physical Sciences and Engineering,
  Australian National University,
  Canberra, ACT 0200
  Australia
List of Contributors

- **Oleg Kidun, Ch. 3**
  Max-Planck Institut für Mikrostrukturphysik
  Weinberg 2,
  06120 Halle
  Germany
  e-mail: okidun@mpi-halle.de

- **Jürgen Kirschner, Ch. 5**
  Max-Planck Institut für Mikrostrukturphysik
  Weinberg 2,
  06120 Halle
  Germany
  e-mail: sekrki@mpi-halle.de

- **Eiichi Kobayashi, Ch. 16**
  Institute of Materials Structure Science, KEK,
  1-1 Oho, Tsukuba 305-0801
  Japan
  e-mail: eiichik@post.kek.jp

- **Azzedine Lahmam-Bennani, Ch. 4**
  Laboratoire des Collisions Atomiques et Moléculaires,
  Bâtiment 351
  Université de Paris-Sud XI,
  F-91405 Orsay cedex
  France
  e-mail: azzedine.l-bennani@lcam.u-psud.fr

- **Andrea Marini, Ch. 2**
  Departamento de Física de Materiales,
  Facultad de Ciencias Químicas,
  Universidad del País Vasco,
  and
  Donostia International Physics Center
  Universidad del País Vasco
  E-20018 San Sebastián,
  Basque Country
  Spain
  e-mail: marini@sc.ehu.es

- **Hans Lischka, Ch. 10**
  Institute for Theoretical Chemistry and Structural Biology
  University of Vienna
  Währinger Straße 17
  A-1090 Vienna
  Austria
  e-mail: Hans.Lischka@univie.ac.at

- **Andrea Liscio, Ch. 14**
  Department of Physics and Unità INFM
  University of Rome, Roma Tre
  Via della Vasca Navale 84
  I-00146 Rome
  Italy
  e-mail: liscio@fis.uniroma3.it
  and
  IMIP-CNR Area della Ricerca di Roma,
  via Salaria Km 29,3
  Montelibretti
  Italy

- **Kazuhiko Mase, Ch. 16**
  Institute of Materials Structure Science, KEK,
  1-1 Oho, Tsukuba 305-0801
  Japan
  e-mail: mase@post.kek.jp

- **Francesco Offi, Ch. 14**
  Department of Physics and Unità INFM
  University of Rome, Roma Tre
  Via della Vasca Navale 84
  I-00146 Rome
  Italy
  e-mail: offi@fis.uniroma3.it

- **Masahide Ohno, Ch. 12**
  Quantum Science Research,
  2-8-5 Tokiwadai,
  Itabashi-ku,
  Tokyo, 174-0071
  Japan
• G. van Riessen,  Ch. 15
  Murdoch University
  Perth, Western Australia

• Alessandro Ruocco,  Ch. 14
  Department of Physics and Unità INFM
  University of Rome, Roma Tre
  Via della Vasca Navale 84
  I-00146 Rome
  Italy
  e-mail: ruocco@fis.uniroma3.it

• Sergej Samarin,  Ch. 6
  School of Physics,
  The University of Western Australia,
  35 Stirling Hwy, Crawley,
  WA 6009,
  Australia
  e-mail: samar@physics.uwa.edu.au

• Vladimir A. Sashin,  Ch. 7
  Atomic and Molecular Physics Laboratories,
  Research School of Physical Sciences and Engineering,
  Australian National University,
  Canberra, ACT 0200
  Australia

• Alex K. See,  Ch. 13
  Chartered Semiconductor Manufacturing
  Technology Development Division
  Singapore 738406
  Singapore

• Anthony David Sergeant,  Ch. 6
  School of Physics,
  The University of Western Australia,
  35 Stirling Hwy, Crawley,
  WA 6009
  Australia

• Wing-Kit Siu,  Ch. 13
  Telcordia Technologies
  1 Telcordia Drive
  Somerset, NJ 08854
  USA
  e-mail: wksiu@physics.rutgers.edu

• Giovanni Stefani,  Ch. 14
  Department of Physics and Unità INFM
  University of Rome, Roma Tre
  Via della Vasca Navale 84
  I-00146 Rome
  Italy
  e-mail: stefani@fis.uniroma3.it

• Stephen M. Thurgate,  Ch. 15
  Murdoch University
  Perth, Western Australia

• Alberto Verdini,  Ch. 14
  National Laboratory TASC-INFM
  Area Science Park
  SS 14 Km 163.5
  I-34012 Basovizza, Trieste
  Italy
  e-mail: verdini@tasc.infm.it

• Maarten Vos,  Ch. 7
  Atomic and Molecular Physics Laboratories,
  Research School of Physical Sciences and Engineering,
  Australian National University,
  Canberra, ACT 0200
  Australia

• Erich Weigold,  Ch. 7
  Atomic and Molecular Physics Laboratories,
  Research School of Physical Sciences and Engineering,
  Australian National University,
  Canberra, ACT 0200
  Australia
  e-mail: erich.weigold@arc.gov.au
List of Contributors

- **James Francis Williams, Ch. 6**
  School of Physics, The University of Western Australia, 35 Stirling Hwy, Crawley, WA 6009 Australia
  e-mail: jfw@cyllene.uwa.edu.au

- **Carsten Winkler, Ch. 5**
  Max-Planck Institut für Mikrostrukturphysik Weinberg 2, 06120 Halle Germany
  e-mail: winkler@mpi-halle.de

- **Helmut Winter, Ch. 11**
  Institut für Physik der Humboldt-Universität zu Berlin, Physik der Grenzflächen und dünnen Schichten Brook-Taylor-Str. 6 12489 Berlin, Germany
  e-mail: winter@physik.hu-berlin.de

- **Ludger Wirtz, Ch. 10**
  Donostia International Physics Center (DIPC) Paseo Manuel de Lardizabal 4 20018 San Sebastián Spain
  and
  Institute for Theoretical Physics Vienna University of Technology Wiedner Hauptstraße 8-10/136 1040 Vienna Austria

- **Hua Yao, Ch. 14**
  Department of Physics and Astronomy and Laboratory of Surface Modification, Rutgers University, 136 Frelinghuysen Road, 08855 Piscataway, New Jersey e-mail: huayao@physics.rutgers.edu
1 A First-Principles Scheme for Calculating the Electronic Structure of Strongly Correlated Materials: GW+DMFT

Ferdi Aryasetiawan, Silke Biermann, and Antoine Georges

1.1 Introduction

The last few decades have witnessed substantial progress in the field of electronic structure of materials. Using density functional theory (DFT) [1,2] within the local density approximation (LDA) or generalized gradient approximation (GGA) [3] it is quite routine to calculate the electronic structure of relatively complicated materials containing tens of atoms per unit cell. The success of LDA, however, is also accompanied by a number of serious problems. It was noticed very early on that, when applied to calculate the band structures of s–p semiconductors and insulators, the band gaps are systematically underestimated by some tens of percents. Apart from the too small gaps, the band dispersions are very reasonable. This remarkable property of the LDA is still waiting for an explanation since formally there is no theoretical justification for identifying the one-particle Kohn–Sham eigenvalues as quasiparticle energies observed in photoemission experiments. Applications to alkali metals also indicate some problems, albeit less serious. When the band dispersions are compared with photoemission data, they are found to be too wide by 10–30%. Some many-body calculations of the electron gas [4, 5], however, suggest that the band widths are actually widened compared with the free-electron values and that the LDA performs better than is commonly believed. If this turns out to be true, photoemission data would presumably need a complete revision. In any case, the LDA errors in s–p metals are probably less significant than the band gap errors in semiconductors and insulators.

A much more serious problem of the LDA arises when it is applied to calculate the electronic structures of so-called “strongly correlated systems”. We have to be more precise with what we mean by correlations. Even in the electron gas, correlation as conventionally defined is rather large. It is as large as exchange so that the two almost cancel each other leaving the free-electron band essentially unchanged. Thus, it is more appropriate in our case to define correlation as anything beyond the LDA rather than anything beyond the Fock exchange since the former is usually our starting point in electronic structure calculations of solids.

Strongly correlated systems are characterized by partially occupied localized orbitals such as found in transition metal oxides or 4f metals. Here the problem is often more of a qualitative rather than a quantitative nature. It is often found that the LDA predicts a transition metal oxide to be a metal whereas experimentally it is an antiferromagnetic insulator. To cite some examples, LaMnO₃, famous for its colossal magnetoresistance, and La₂CuO₄, a well-known parent compound of high-temperature superconductors, are antiferromagnetic insulators but
predicted to be metals by the LDA [6]. In cases where the LDA does predict the correct structure, it is legitimate to ask if the one-particle spectrum is also reproduced correctly. According to the currently accepted interpretation, transition metal oxides may be classified as charge-transfer insulators [7,8], which are characterized by the presence of occupied and unoccupied 3d bands with the oxygen 2p band in between. The gap is then formed by the oxygen 2p and unoccupied 3d bands, unlike the gap in LDA, which is formed by the 3d states (Mott–Hubbard gap). A more appropriate interpretation is to say that the highest valence state is a charge-transfer state: During photoemission a hole is created in the transition metal site but due to the strong 3d Coulomb repulsion it is energetically more favorable for the hole to hop to the oxygen site despite the cost in energy transfer. A number of experimental data, notably 2p core photoemission resonance, suggest that the charge-transfer picture is more appropriate to describe the electronic structure of transition metal oxides. And of course in the case of 4f metals, the LDA, being a one-particle theory, is totally incapable of yielding the incoherent part of the spectral function or satellite structures.

The above difficulties encountered by the LDA have prompted a number of attempts at improving the LDA. Notable among these is the GW approximation (GWA), developed systematically by Hedin in the early sixties [9]. He showed that the self-energy can be formally expanded in powers of the screened interaction $W$, the lowest term being $iGW$, where $G$ is the Green function. Due to computational difficulties, for a long time the applications of the GWA were restricted to the electron gas but with the rapid progress in computer power, applications to realistic materials eventually became possible about two decades ago. Numerous applications to semiconductors and insulators reveal that in most cases the GWA [10,11] removes a large fraction of the LDA band-gap error. Applications to alkali metals show band narrowing from the LDA values and account for more than half of the LDA error (although controversy about this issue still remains [12]).

The success of the GWA in sp materials has prompted further applications to more strongly correlated systems. For this type of materials the GWA has been found to be less successful. For example, GW calculation on nickel [13] does reproduce the photoemission quasiparticle band structure rather well, as compared with the LDA one where the 3d band width is too large by about 1 eV, but the too large LDA exchange splitting of 0.6 eV (experimentally 0.3 eV) remains essentially unchanged. Moreover, the famous 6 eV satellite is not reproduced.

Application to NiO [14], a prototype of transition metal oxides, also reveals some shortcomings. One problem is related to the starting Green’s function, usually constructed from the LDA Kohn–Sham orbitals and energies. In the LDA the band gap is very small, about 0.2 eV compared with the 4 eV experimental band gap. A commonly used procedure of performing a one-iteration GW calculation yields about 1 eV gap, much too small. This problem is solved by performing a partial self-consistency, where knowledge of the self-energy from the previous iteration is used to construct a better starting one-particle Hamiltonian [14]. This procedure improves the band gap considerably to a self-consistent value of 5.5 eV and at the same time increases the LDA magnetic moment from 0.9 $\mu_B$ to about 1.6 $\mu_B$ much closer to the experimental value of 1.8 $\mu_B$. However, the GWA maintains the Mott–Hubbard gap, i.e., the gap is formed by the 3d states as in the LDA, instead of the charge-transfer gap. In other words, the top of the valence band is dominated by the Ni 3d. A more recent calculation using a more refined procedure of partial self-consistency has also confirmed these results [15]. The
1.1 Introduction

Problem with the GWA appears to arise from inadequate account of short-range correlations, probably not properly treated in the random-phase approximation (RPA).

Attempts at improving the LDA to treat strongly correlated systems were initiated by the LDA+U method [16–19], which introduces, on top of the LDA Hamiltonian, a Hubbard U term and a double-counting correction term, usually applied to partially filled 3d or 4f shells. The LDA+U method is essentially a Hartree–Fock approximation to the LDA+U Hamiltonian. In the LDA, the Kohn–Sham potential does not explicitly distinguish between occupied and unoccupied orbitals so that they experience the same potential. In, for example, transition metal oxides, where the 3d orbitals are partially occupied, this leads to metallic or underestimation of the band gap. The LDA+U cures this problem by approximately pushing down the occupied orbitals by \( \frac{U}{2} \) and pushing up the unoccupied orbitals by \( \frac{U}{2} \), creating a lower and upper Hubbard band, thus opening up a gap of the order of the Hubbard U. The LDA+U method has been successfully applied to late transition metal oxides, rare earth compounds such as CeSb, as well as to problems involving metal–insulator transition and charge-orbital ordering.

More recently, the idea of the LDA+U was extended further by treating the Hubbard U term in a more sophisticated fashion utilizing the dynamical mean-field theory (DMFT) [20]. The DMFT is remarkably well suited for treating systems with strong on-site correlations because the on-site electronic Coulomb interactions are summed to all orders. This is achieved by using a mapping onto a self-consistent quantum impurity problem, thereby including the effects of the surrounding in a mean-field approximation. The strength of the DMFT is its ability to properly describe Mott phenomenon or the formation of local moments, which is the key to understanding many physical properties in strongly correlated materials. The combination of LDA and DMFT takes advantage of the first-principles nature of LDA while at the same time incorporates local correlation effects not properly treated within the LDA. The LDA+DMFT method [19, 21, 22] has now been successfully applied to a number of systems.

In both the LDA+U and LDA+DMFT methods, two fundamental problems remain unaddressed. First, the Hubbard U is usually treated as a parameter, and second, the Hubbard U term contains interaction already included in the LDA but it is not clear how to take into account this double-counting term in a precise way. Thus, a truly first-principles theory for treating strongly correlated systems is still lacking. In this chapter, we describe a dynamical mean-field approach for calculating the electronic structure of strongly correlated materials from first-principles [23, 24]. The DMFT is combined with the GW method, which enables one to treat strong interaction effects [25]. One of the main features of the new scheme is that the Hubbard U is calculated from first principles through a self-consistency requirement on the on-site screened Coulomb interaction, analogous to the self-consistency in the local Green’s function in the DMFT. Since the GWA has an explicit diagrammatic representation, the on-site contribution of the GW self-energy can be readily identified and the scheme then allows for a precise double-counting correction.

In the next two sections, we will give a summary of the GWA and DMFT, describing their main features. In the fourth section we lay out the GW+DMFT scheme, followed by a simplified application of the scheme to the excitation spectrum of nickel. Finally we discuss some future challenges and directions.
1.2 The \textit{GW} Approximation

1.2.1 Theory

It can be shown that the self-energy may be expressed as \cite{[9]}

\[ \Sigma(1, 2) = -i \int d^3 v(1, 4) G(1, 3) \frac{\delta G^{-1}(3, 2)}{\delta \phi(4)} \]  

where \( v \) is the bare Coulomb interaction, \( G \) is the Green function and \( \phi \) is an external time-dependent probing field. We have used the short-hand notation \( 1 = (x_1 \, t_1) \). From the equation of motion of the Green function

\[ G^{-1} = i \frac{\partial}{\partial t} - H_0 - \Sigma \]  

\[ H_0 = h_0 + \phi + V_H \]

\( h_0 \) is the kinetic energy and \( V_H \) is the Hartree potential. We then obtain

\[ \frac{\delta G^{-1}(3, 2)}{\delta \phi(4)} = -\delta(3 - 2) \left[ \delta(3 - 4) + \frac{\delta V_H(3)}{\delta \phi(4)} \right] - \frac{\delta \Sigma(3, 2)}{\delta \phi(4)} \]

\[ = -\delta(3 - 2) \epsilon^{-1}(3, 4) - \frac{\delta \Sigma(3, 2)}{\delta \phi(4)} \]  

(1.4)

where \( \epsilon^1 \) is the inverse dielectric matrix. The GWA is obtained by neglecting the vertex correction \( \delta \Sigma/\delta \phi \), which is the last term in Eq. (1.4). This is just the random-phase approximation (RPA) for \( \epsilon^{-1} \). This leads to

\[ \Sigma(1, 2) = i G(1, 2) W(1, 2) \]  

where we have defined the screened Coulomb interaction \( W \) by

\[ W(1, 2) = \int d^3 v(1, 3) \epsilon^{-1}(3, 2) \]  

(1.6)

The RPA dielectric function is given by

\[ \epsilon = 1 - v P \]  

(1.7)

where

\[ P(r, r'; \omega) = -2i \int \frac{d\omega'}{2\pi} G(r, r'; \omega + \omega') G(r', r; \omega') \]

\[ = 2 \sum_{\text{occ}} \sum_{\text{unocc}} \psi_i^\dagger(r) \psi_j^\dagger(r') \psi_j(r) \psi_i(r') \]

\[ \times \left\{ \frac{1}{\omega - \epsilon_j + \epsilon_i + i\delta} - \frac{1}{\omega + \epsilon_j - \epsilon_i - i\delta} \right\} \]  

(1.8)
with the Green function constructed from a one-particle band structure \( \{ \psi_i, \varepsilon_i \} \). The factor of 2 arises from the sum over spin variables. In frequency space, the self-energy in the GWA takes the form

\[
\Sigma(r, r'; \omega) = \int \frac{d\omega'}{2\pi} e^{i\omega' \omega} G(r, r'; \omega + \omega') W(r, r'; \omega')
\]  

We have so far described the zero temperature formalism. For finite temperature we have

\[
P(r, r'; i\nu_n) = \frac{2}{\beta} \sum_{\omega_k} G(r, r'; i\nu_n + i\omega_k) G(r', r; i\omega_k)
\]

\[
\Sigma(r, r'; i\omega_n) = -\frac{1}{\beta} \sum_{\nu_k} G(r, r'; i\omega_n + i\nu_k) W(r, r'; i\nu_k)
\]

In the Green function language, the Fock exchange operator in the Hartree–Fock approximation (HFA) can be written as \( iGv \). We may therefore regard the GWA as a generalization of the HFA, where the bare Coulomb interaction \( v \) is replaced by a screened interaction \( W \). We may also think of the GWA as a mapping to a polaron problem where the electrons are coupled to some bosonic excitations (e.g., plasmons) and the parameters in this model are obtained from first-principles calculations.

The replacement of \( v \) by \( W \) is an important step in solids where screening effects are generally rather large relative to exchange, especially in metals. For example, in the electron gas, within the GWA, exchange and correlation are approximately equal in magnitude, to a large extent canceling each other, modifying the free-electron dispersion slightly. But also in molecules, accurate calculations of the excitation spectrum cannot neglect the effects of correlations or screening. The GWA is physically sound because it is qualitatively correct in some limiting cases [26].

### 1.2.2 The GW Approximation in Practice

The quality of the GWA may be seen in Figure 1.1, where a plot of band gaps of a number of well known semiconductors and insulators is displayed. It is clear from the plot that the LDA systematically underestimates the band gaps and that the GWA substantially improves the LDA band gaps. It has been found that for some materials, like MgO and InN, significant error still remains within the GWA. The reason for the discrepancy has not been understood well. One possible explanation is that the result of the one-iteration GW calculation may depend on the starting one-particle band structure. For example, in the case of InN, the starting LDA band structure has no gap. This may produce a metal-like (over)screened interaction \( W \) which fails to open up a gap or yields too small a gap in the GW calculation. Similar behavior is also found in the more extreme case of NiO, where a one-iteration GW calculation only yields a gap of about 1 eV starting from an LDA gap of 0.2 eV (the experimental gap is 4 eV) [10, 14].

The problems with the GWA arise when it is applied to strongly correlated systems. Application to ferromagnetic nickel [13] illustrates some of the difficulties with the GWA. Starting from the LDA band structure, a one-iteration GW calculation does improve significantly the LDA band structure. In particular it reduces the too large 3d band width bringing it into...
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Figure 1.1: Band gaps of some selected semiconductors and insulators calculated within the GWA compared with the LDA and experimental values. The GW data are taken from [27].

much better agreement with photoemission data. However, the too large LDA exchange splitting (0.6 eV compared with the experimental value of 0.3 eV) remains essentially unchanged. Moreover, the famous 6 eV satellite, which is of course missing in the LDA, is not reproduced. These problems point to deficiencies in the GWA in describing short-range correlations since we expect that both exchange splitting and satellite structure are influenced by on-site interactions. In the case of exchange splitting, long-range screening also plays a role in reducing the HF value and the problem with the exchange splitting indicates a lack of spin-dependent interaction in the GWA: In the GWA the spin dependence only enters in $G$ not in $W$.

Application to NiO, the prototype of Mott–Hubbard transition metal oxides, reveals another difficulty with the one-iteration GWA. As already mentioned previously, when the starting band structure is far from the experimental quasiparticle band structure, a one-iteration GW calculation may not be sufficient. This problem may be circumvented by performing a partial self-consistent calculation in which the self-energy from the previous iteration at a given energy, such as the Fermi energy of the center of the band of interest, is used to construct a new set of one-particle orbitals. This procedure is continued to self-consistency such that the starting one-particle band structure gives zero self-energy correction [10, 14, 15]. A more serious problem, however, is describing the charge-transfer character of the top of the valence band. The GWA essentially still maintains the Mott–Hubbard band gap as in the LDA, i.e., the top of the valence band is mainly of 3d character rather than the charge-transfer character dominated by the 2p oxygen hole. As in nickel, the problem with the satellite arises again. Depending on the starting band structure, a satellite may be reproduced albeit at a too high energy. Thus there is a strong need to improve the short-range correlations in the GWA which may be achieved by using a suitable approach based on the dynamical mean-field theory described in the next section.