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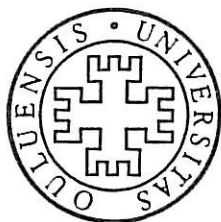
PHYSICA No. 29

LOCAL-DENSITY ELECTRONIC
STRUCTURE CALCULATIONS
ON THE SPECTRA AND
REACTIVITY OF METALS

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Abstract

This thesis deals with the electronic structure calculation methods at the level of local-density approximation. Electronic structures are evaluated for various systems involving mostly metals; ranging from free atoms and clusters to bulk solid and surfaces. New models and computational methods are also developed. The role of the electronic structure behind the properties of matter is emphasized, and especially, the unique properties of the conduction electron response are examined and compared to the transitions in free atoms. The role of spin-polarisation is found to be essential with large-effects on the x-ray edge exponents, line shapes and solid state shifts in photoelectron and Auger electron spectra. The chemical reactivity of small metal clusters and metal surfaces is examined, and it is shown that the reactivity can be traced back to the local Fermi level electronic structure. In particular, the energy dissipation in adsorption onto metal surfaces is studied. Finally, a new computational procedure for the total energy within LCAO is tested through the evaluation of potential curves and the consequent spectroscopic data of diatomic molecules. The general conclusion is that the local-density approximation makes both qualitative and quantitative electronic structure calculations feasible in the whole field from free atoms to solid matter. Thus, it can be used in applications from sophisticated spectroscopy to practical chemistry, but nevertheless, retained within the same simple formalism.

Key words: jellium model, cluster, photoelectron and Auger spectroscopy, surface physics, catalysis, electron-hole pairs

PREFACE

This thesis belongs to both theoretical and computational physics, and theoretical or quantum chemistry. It has been a pleasant and instructive work for a number of reasons. It deals with the first principles methods for finding electronic structures, which in practice means evaluation of the motion and energies of electrons within the formalism of quantum theory. The quantum theory has opened up new views in research beyond the conventional spectroscopist's cook-book quantum mechanics, thereby making the work interesting, challenging and sometimes even exotic, but simultaneously also laborious at the practical level. Furthermore, the use of various physical approximations, numerical methods and high capacity computers has offered a wide and rich research field to work in; which has taught me a lot. On the other hand, this work has also taught me that the more one learns the better one sees the modesty of his own knowledge.

October 1986

The Author

LIST OF ORIGINAL PAPERS

The present thesis consists of an introductory part and the following seven papers:

- I T.T. Rantala, *Spin-density calculations for core-electron photoemission and Auger electron line shapes, x-ray-edge exponents, and solid-state shifts*, Phys. Rev. B **28**, 3182 (1983).
- II J. Väyrynen, T.T. Rantala, E. Minni and E. Suoninen, *Anomalous Auger-electron spectra of metallic calcium*, J. Electron Spectrosc. Relat. Phenom., **31**, 293 (1983).
- III T.T. Rantala, *Form factors of metallic aluminium from atom-in-jellium-vacancy model*, J. Phys. F: Metal. Phys., accepted.
- IV A. Rosén and T.T. Rantala, *Analysis of the Reactivity of Small Cobalt Clusters*, Z. Phys. D - Atoms, Molecules and Clusters **3**, 205 (1986).
- V T.T. Rantala, A. Rosén and B. Hellsing, *A finite cluster approach to the electron-hole pair damping of the adsorbate vibration: CO adsorbed on Cu(100)*, J. Electron Spectrosc. Relat. Phenom., **39**, 173 (1986).
- VI T.T. Rantala and A. Rosén, *Electronic damping of adsorbate motion: CO vibration on the Cu(100) surface*, Phys. Rev. B **34**, 837 (1986).
- VII T.T. Rantala, B. Wästberg and A. Rosén, *Potential energy curves for diatomic molecules calculated with numerical basis functions*, Chem. Phys., **109**, 261 (1986).

These papers are referred to in the text by the above Roman numerals.

The papers II and IV-VII were prepared in co-operation with other authors. In papers II and IV the present author is responsible for the electronic structure calculations and the relevant part of the text. With regard to papers V and VI the author is responsible for the idea of describing electron-hole pairs in a finite cluster, all the calculations and writing of the papers. The author's contribution in the last paper concerns the development of the total energy procedure, its coding and also the writing of the corresponding part of the manuscript, whereas the practical computations were carried out by B. Wästberg. However, the present author takes responsibility for errors and incompleteness possibly remaining in the included works.

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SELOSTUS VÄITÖSKIRJASTA

Väitöskirja on lähinnä materiaalfysiikan aihepiiriin kuuluva tutkimus, jossa tarkastellaan pääasiassa metallien ominaisuuksia teoreettisesti ja numeeristen laskumenetelmien avulla. Metalleja tarkastellaan vapaina atomeina, pieninä molekyylien kaltaisina ryppäinä eli "klustereina" sekä kiinteässä olomuodossaan. Tutkimuskohteina ovat em. eri esiintymismuotojen vaikutukset sekä atomien sisempään että ulompaan elektroniverhoon, joka määrää aineiden kemialliset ominaisuudet. Erityisesti tarkastellaan eräitä metallien spektrejä sekä pienten metalliklustereiden ja metallipintojen reaktiivisuutta ja kemiallisia ominaisuuksia esimerkiksi katalyytteinä.

Ratkaisemalla aineen elektronirakenne saadaan tietoa aineen ominaisuuksista "teoreettisesti", ilman kokeellisia mittauksia, ja samalla voidaan selvittää kyseisiin ominaisuuksiin johtavat perimmäiset syyt. Käytännössä teoreettista tarkastelua ja numeerisia laskuja vaikeuttavat elektronien suuri lukumäärä ja erityisesti atomaarista kokoa pienempien hiukkasten tarkasteluun tarvittavat menetelmät. Elektronitilat onkin ratkaistava kvanttifysiikan (kvanttikemian) menetelmin, mikä johtaa välttämättä yksinkertaistuksiin ja numeerisiin ratkaisumenetelmiin. Tämän tutkimuksen numeeriset laskut on tehty suurilla ja tehokkailla tietokoneilla Suomessa ja ulkomailla. Käytettyjen menetelmien kehittäminen on ollut osa tutkimusta, ja yhtenä tarkoituksena on ollut myös selvittää tämän hetken laskumenetelmien pystyvyyttä käytännön ongelmien ratkaisemiseen.

Työssä tarkastellaan yksityiskohtaisesti kiinteän olomuodon vaikutuksia useiden metallien elektronisiin siirtymiin (transitioihin) ja niistä aiheutuvia röntgenkynnyksen muotoja sekä elektronispektrien viivojen muotoja ja energioita. Litium- ja kalsiummetallien tapauksissa löydettiin uutena ilmiönä siirtymiä varjostavan varauksen voimakas spin-polarisaatio. Kiinteän olomuodon vaikutusten huomioon ottamiseksi kehitettiin myös uutta menetelmää, jota testattiin laskemalla alumiinimetallin elektronitiheysprofiili ja sitä vastaavat kokeelliset röntgensironnan muototekijät.

Pienten kobolttiklustereiden reaktiivisuudessa kokeellisesti havaittu koosta riippuva vaihtelu selitetään tutkimuksessa koon mukana muuttuvan elektronirakenteen seurauksena. Tutkittaessa hiilimonoksidin adsorptiota kuparipinnalle voitiin selittää eräs katalysoiduissa reaktioissa tärkeä energianvaihtomekanismi ja lisäksi määritettiin tämän mekanismin tehokkuus. Tällaisten reaktioiden dynamiikan tarkastelua varten kehitettiin laskumenetelmää, jota testattiin eräille kaksiatomisille molekyyileille tunnettujen kokeellisten tulosten avulla.

Yleisenä johtopäätöksenä voidaan sanoa, että elektronirakennelaskujen tarkkuus riittää jo nykyisin antamaan luotettavasti tietoa useiden aineiden ominaisuuksista perustutkimuksen tarpeiden lisäksi myös monia käytännön sovellutuksia varten. Merkittävää on myös, että aineiden ominaisuuksien määrittäminen tällä tavoin on mahdollista silloinkin, kun se kokeellisesti on vaikeaa tai kallista, tai jopa teknisesti mahdotonta.

ERRATUM

RANTALA, TAPIO T, Local-density electronic structure calculations on the spectra and reactivity of metals

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Key words: jellium model, cluster, photoelectron and Auger spectroscopy, surface physics, catalysis, electron-hole pairs

1. INTRODUCTION

In this chapter we will first give some background for this work and briefly review the field of electronic structure calculation methods. In the next chapter the quantum mechanical background relevant to this work is briefly reviewed. The many-body aspects in electron-electron interactions are discussed, and in particular, the local-density approximation is defined. Chapter 3 deals with the two models, which we use for the structure of matter, and the numerical approaches for solving the Schrödinger equation. Chapter 4 contains the applications and discussions, and the conclusions are presented in the last chapter. A more detailed analysis of the methods and results is found in the included original papers.

1.1. Electronic structure and properties of matter

The macroscopic properties of matter are based on the microstructure of the material. Matter consists of molecules or crystals, and ultimately of atoms, which are the building blocks of all matter. Therefore, from the constituent atoms we can build any macroscopic system and from the chemistry of atoms we can often predict its properties, too. To be strict, however, we need to evaluate the electronic structure of the whole system in order to derive the properties from their origins (*ab initio*). In practice this leads to a laborious evaluation of the "motion" of electrons using the quantum theory and the many-body technique.

However, the description of a system at the level of electrons and nuclei allows us to begin with the least possible information and the first principles. Masses, charges and basic interactions of electrons and nuclei are well known and we may invoke quantum mechanics to write the hamiltonian and the equation of motion (the Schrödinger equation) for the system considered and solve it as perfectly as possible. The application of the minimum energy principle then leads to stationary systems. Even though the hamiltonian is well known, there remain considerable problems in solving the Schrödinger equation.

The many-body problem of a large number of electrons is too complex to be solved exactly, even in classical mechanics let alone in quantum mechanics. In Chapter 2 we will return to these many-body aspects in more detail and in Chapter 3 the two basic approaches for solving the Schrödinger equation are described. The level of approximation to be chosen depends on the complexity and extent of the system considered, the accuracy required and the computational capacity available. Therefore, there exist a large number of *ab initio* and also semi-empirical methods, ranging from high accuracy special purpose methods to those of a wide range of applicability [1-15].

There are a number of possibilities for direct applications of the electronic structure

calculations for evaluation of the properties of matter. Just to mention a few we have the geometry of molecules or cohesion and phase transitions of solids, optical properties, electric and thermal properties of insulators, semiconductors and metals. For calculated properties of bulk metals see e.g. the book of Moruzzi *et al.* ^[4]. Catalysis, corrosion and whole surface physics and chemistry are also explainable by the electronic structures. Furthermore, all the spectroscopic data for atoms, molecules and solid materials are available from *ab initio* electronic structure calculations to continually increasing accuracy.

1.2. Electronic structure calculation methods

Free atoms are the simplest electron systems in nature. Their spherical symmetry simplifies the theoretical approaches significantly and makes high accuracy results attainable with moderate efforts. Depending on the element, the Hartree-Fock (HF) ^[10], Multi-Configuration-HF (MCHF) ^[10-11] or the relativistic Multi-Configuration-Dirac-Fock (MCDF) ^[12-13] methods should be chosen. The free atom results from local-density calculations presented in this work are also reasonably accurate and the non-local corrections ^[27] improve the atomic results even to higher accuracy than that of HF.

The relatively high symmetry of diatomic molecules can also be taken advantage of in calculations and high accuracy numerical results are attainable today ^[14-15]. However, with regard to the evaluation of the wave functions for larger molecules the lower symmetry forces one to invoke other methods. One may employ the Linear Combination of Atomic Orbitals (LCAO) with analytical Slater Type Orbitals (STO), Gaussian Type Orbitals (GTO) or fully numerical atomic orbitals ^[17,17]. The inclusion of correlations in high accuracy molecular calculations is essential ^[11].

Solids consist of a huge number of interacting atoms ($\sim 10^{23}$) and therefore they are usually studied with certain simplifying assumptions in theoretical approaches. Macroscopically, solids are assumed to be homogeneous but at the microscopic level the solid phase of matter is modelled as a periodic and infinite array of atoms. The translational symmetry of the periodic lattice is reflected in the electronic structure; the conduction electron states of metals being a good example. Plane waves are a natural basis for a theoretical description of such extended periodic structures; as exemplified by the Orthogonalized-Plane-Waves (OPW) and the Augmented-Plane-Waves (APW) methods. In these methods and their derivatives either core electron states are described by a pseudopotential "orthogonalizing" the plane waves to the core or plane waves are augmented to inner regions of atoms to describe the core electrons ^[5]. The effect of the cores can be taken into account through pseudopotentials ^[16], if only valence electrons are of interest.

Another way is to start from the (nearly) spherical core of atoms and extend their electronic wavefunctions to the interstitial region as is done in the Korringa-Kohn-Rostoker (KKR) or LCAO type methods. The Linear Combination of Muffin-Tin Orbitals (LMTO) procedure, which originates from both LCAO and KKR, divides the space into two regions; the muffin-tin spheres containing the ion cores and the remaining interstitial region. It is, as such, an effective method for periodic structures. Non-periodic structures such as molecules, surfaces and adsorbates, and disordered

solids are better handled with LCAO, which is very flexible in geometry. LCAO or Tight-Binding (TB) methods are also good in describing localized electrons and oriented bonding, which are met in semiconductors and insulators [5].

The simplest description of a metal is the jellium model, where the periodicity is ignored: the ion cores are smeared to a constant positive background charge and the conduction electrons form a neutralizing homogeneous electron gas. Obviously, it is not a fruitful model to study the metallic electron states themselves, but it is a good model to reveal trends and foremost geometrically simple, which makes accurate numerical solutions possible. The atom-in-jellium-vacancy model, which is also used in this work, is an effective approach in the examination of the interactions between core and conduction electrons of metals. It includes all the electrons in a metal and is spherically symmetric thereby offering a computationally simple way to evaluate of the properties of metals [1-11].

2. QUANTUM MECHANICAL BACKGROUND

2.1. The Schrödinger equation

At the end of the last century classical physics was a well developed theory for macroscopic phenomena. The spectrum of black body radiation, photoelectric effect and atomic spectra were the first observations which conflicted with classical physics. It initiated intensive theoretical work by several contributors, resulting in the development and formulation of the quantum theory during 1900 – 1930 [17]. The new theory led to entirely new concepts, namely the wave nature of particles and the consequent quantization of particle energies through the boundary conditions of standing waves. It also led to the uncertainty principle and even new philosophies — in physics at least.

The dual particle-wave nature of an electron leads to its description with a wave function $\psi(\mathbf{r}, t)$: a function of space coordinates and time. It is the solution of the Schrödinger equation and contains all the information on the time evolution and the particle "motion" in space; also in a stationary, time-independent state.

The non-relativistic Schrödinger equation for an electron in a stationary state (in atomic units, where $m = e = \hbar = a = 4\pi\epsilon_0 = 1$ and the energy appears in Hartrees = 27.2116 eV) is written as

$$\hat{h}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad (2.1)$$

where the hamiltonian is

$$\hat{h}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) \quad (2.2)$$

and $v(\mathbf{r})$ is the potential felt by the electron. The two contributions in the hamiltonian (2.2) are the kinetic energy and the potential energy, respectively. Boundary conditions of the wave function lead to an eigenvalue problem and a set of solutions ψ_i corresponding to discrete eigenenergies ϵ_i .

The wave function gives the probability density of the particle

$$\rho(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r}), \quad (2.3)$$

for which

$$\int_V \rho(\mathbf{r}) d\mathbf{r} = 1 \quad (2.4)$$

is the normalization condition in space V .

2.2. Many-electron systems

Resorting to the Born-Oppenheimer approximation and including only electrostatic Coulomb interactions, the hamiltonian of N electrons, at the presence of M nuclei, becomes

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i,\nu}^{N,M} \frac{-Z_\nu}{|\mathbf{r}_i - \mathbf{R}_\nu|} + \sum_{i < j}^N \frac{1}{r_{ij}}, \quad (2.5)$$

where Z_ν and $\mathbf{R}_\nu$ are the charges and positions of the nuclei ν , and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ are the distances between two electrons i and j . The many-electron wave function must then satisfy the Schrödinger equation

$$\hat{H}\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_k \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (2.6)$$

with the relevant boundary and normalization conditions.

The indistinguishability of identical particles leads to symmetry requirements of the many-particle wave function, and for electrons (generally for fermions) the wave function must be antisymmetric. The antisymmetrized product of one-electron spin-orbitals

$$\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{A}(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_N(\mathbf{r}_N)) \quad (2.7)$$

is the simplest approximation to the many-electron function. The antisymmetry requirement was first found as an experimental fact when interpretation of atomic spectra led Slater to introduce the determinantal combination of (orthonormal) one-electron functions

$$\Psi^{HF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.8)$$

which is a convenient way of antisymmetrizing the many-electron wave function [18-20]. This is also the theoretical basis behind the Hartree-Fock (HF) approximation [19,20].

If the electronic interactions are included in an average way above, the many-electron Schrödinger equation separates into one-electron contributions, resulting in a one-electron picture of the many-electron system. The one-electron equations are obtained applying the variational principle to the total energy, where the one-electron eigenvalues are Lagrange multipliers assuring the orthonormality of the orbitals. An example is the central field approximation for atoms, which makes numerical, self-consistent, HF calculations for free atoms feasible. Similarly, the average interelectronic potentials are used to separate the many-electron hamiltonian of molecules and metal crystals.

Going beyond the average field models we consider the many-body effects, which are often called just correlations. We are not able to separate the Schrödinger equation any longer and the one-electron spin-orbitals lose their strict meaning. However, the concept of a determinantal configuration state function (2.8) is a useful tool, because the many-body wave function can be expanded as a Multi-Configuration HF (MCHF) wave function

$$\Psi^{MCHF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_k C_k \Psi^{HF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2.9)$$

The MCHF expansion may consist of a large number of configurations, from two to several millions, and high accuracy is obtained only through large scale computations; even for atoms and small molecules.

For very large molecules, clusters or solids these types of methods are not feasible due to the computational capacity required. Furthermore, for infinitely large electron systems like conduction electrons of metals the underlying HF approximation leads to theoretical problems in the form of unphysical singular Fermi velocity arising from the long-range exchange interaction. It leads to a zero density of states at the Fermi surface, and hence to incorrect behaviour of the electronic heat capacity, for example. But these fundamental problems can be circumvented by a reformulation of the theory, and in the next section we present an alternative approach to the many-body problem with a larger range of applicability.

2.3. Density-Functional theory

The alternative approach to the many-electron Schrödinger equation (2.6), namely the Density-Functional Theory (DFT), was introduced by Hohenberg, Kohn and Sham [21,22], and preceeded by the works of Thomas and of Fermi [23], Slater [8,24] and Gáspár [25]. The DFT starts with the ground state one-electron density $\rho(\mathbf{r})$ as a fundamental variable, which has one-to-one correspondence (to within a constant) with the external potential of electrons [21]. The density also gives the total number of electrons N , which then implies that the total energy of the many-electron system is a functional of ρ , and furthermore, the total energy functional has a minimum equal to the ground-state energy of the system [21]. This leads to the conclusion that the ground state density $\rho(\mathbf{r})$ unequivocally determines the entire hamiltonian (2.5).

We decompose the total energy of electrons (a functional of the density ρ) as

$$E[\rho] = T[\rho] + \int \rho(\mathbf{r})v_n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r})v_e(\mathbf{r})d\mathbf{r} + E_{xc}[\rho], \quad (2.10)$$

where $T[\rho]$ is the kinetic energy of N non-interacting electrons in the effective potential v_{eff} , and the two integrals are Coulomb energies of the charge density in the fields of nuclei and the charge density itself, respectively. The last term contains all the remaining contributions, which we call exchange and correlation energy. We point out that due to the definition of the first term, $T[\rho]$, there remains a substantial part of the kinetic energy included in the last term, $E_{xc}[\rho]$.

The variational principle applied to this total energy expression under the constraint of electron conservation now leads to the following self-consistent one-electron like equations [22]

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.11)$$

with

$$v_{eff}(\mathbf{r}) = v_n(\mathbf{r}) + v_e(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2.12)$$

and

$$\rho(\mathbf{r}) = \sum_i q_i |\psi_i(\mathbf{r})|^2, \quad (2.13)$$

where q_i , the occupation number of one-electron levels, is zero for other than the N lowest levels. The external potential

$$v_n(\mathbf{r}) = \sum_{\nu}^M \frac{-Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}|} \quad (2.14)$$

arises from the positively charged nuclei and

$$v_e(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.15)$$

is the Hartree potential of the charge density. The last term in the effective potential (2.12) is the functional derivative of the exchange and correlation energy $E_{xc}[\rho]$ as follows

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (2.16)$$

Using Eqs. (2.10) - (2.13) we may write an alternative expression for the total energy

$$E[\rho] = \sum_i q_i \epsilon_i - \frac{1}{2} \int \rho(\mathbf{r}) v_e(\mathbf{r}) d\mathbf{r} - \int \rho(\mathbf{r}) v_{xc}(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho], \quad (2.17)$$

which does not contain an explicit reference to the kinetic energy.

This approach to the many-electron problem deserves a closer discussion, especially as compared to the HF and MCHF approaches. First of all the DFT presented here is exact with respect to the many-body correlations, at the same level with the infinite order MCHF. However, the one-electron equations look even simpler than the corresponding HF equations. This is an artifact, of course; the many-body effects (neglected in HF but included in MCHF) are only transferred to the unknown functional $E_{xc}[\rho]$. It turns out, however, that there exist accurate approximations to this functional [26-37] and even the simplest one is very useful in making computational methods effective but still reasonably accurate, especially for large or infinite electron systems.

Some further features of the DFT deserve to be mentioned. The one-electron eigenfunctions and eigenvalues in (2.11) do not correspond to those of HF, and they are often regarded only as auxiliary quantities yielding the charge density and the kinetic energy contribution. This looks analogous to the MCHF, where the one-electron picture of the HF approximation with well defined one-electron quantum numbers is lost and the quasi-particle picture emerges. However, for the highest occupied level of a many-electron system it can be shown that the bare DFT eigenvalue equals the ionization energy [26] and the more localized the orbitals are, the more their eigenvalues deviate from the ionization energies. It is interesting to compare this with the self-interaction free eigenvalues of HF approximation, which always differ, and even in the opposite direction, from the ionization energies. We should also note the definitions of the kinetic energy and the Hartree potential in (2.10) and the difference between the corresponding energy contributions in the HF approximation.

2.4. Local-Density approximation

The system of Equations (2.10) - (2.17) is not closed until a formula is found for the unknown functional $E_{xc}[\rho]$. Making use of the properties of a homogeneous electron

gas the useful Local-Density Approximation (LDA) to the exchange and correlation of a many-electron system can be defined.

The exchange is usually defined in terms of HF approximation separating the whole functional into two contributions

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (2.18)$$

where the first term, which is called the exchange energy, is a consequence of the antisymmetry of the total wave function. The second term includes the remaining dynamical correlations, i.e. the many-body effects.

The homogeneous electron gas is defined by its density, ρ , or the density parameter

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{3}}, \quad (2.19)$$

which is the radius of the spherical volume occupied by one electron. Using this, the (average) exchange energy per electron is

$$\varepsilon_x(\rho) = -\frac{3}{4}\left(\frac{3\rho}{\pi}\right)^{\frac{1}{3}} = -\frac{0.458}{r_s}, \quad (2.20)$$

which is obtained analytically by integrating over the wave vector up to the Fermi level. The density dependence is shown graphically in Fig. 2.1.

The correlation energy for the homogeneous electron gas is more laborious to evaluate and a comprehensible discussion of various approximations is given by Hedin and Lundqvist [29]. The two leading terms in the high-density expansion for the ground state [30] are

$$\varepsilon_c(\rho) = 0.0311 \ln r_s - 0.048, \quad (2.21)$$

and other results for a larger range of densities with useful parametrizations are given in the literature [31–33]. The most accurate results for a wide range of electron densities have been evaluated by Monte Carlo simulations of Ceperley and Alder [34], and useful interpolation formulae to these data have been given by Vosko *et al.* [35], and Perdew and Zunger [36].

The exchange-correlation energy per electron in a homogeneous electron gas and its two contributions are shown graphically in Fig. 2.1. They are both negative, which lowers the total energy and stabilizes the electron system. The correlation energy is the smaller of the two and it has a weaker density dependence. The (average) kinetic energy per electron is also shown in the same figure for comparison.

The effective potentials corresponding to the one-electron exchange and correlation energies are obtained using Eqs. (2.16) and (2.20). The exchange potential appears to be

$$v_x(\rho) = -\left(\frac{3\rho}{\pi}\right)^{\frac{1}{3}} \quad (2.22)$$

and the correlation contribution can be included by writing [37]

$$v_{xc} = \beta(r_s) v_x(\rho), \quad (2.23)$$

where $\beta(r_s)$ is a slowly varying function of the density parameter r_s . From the high-density limit $r_s = 0$, $\beta(r_s)$ starts from the value 1 and increases monotonically towards values in the range 1.2 – 1.3 for metallic electron densities [37].

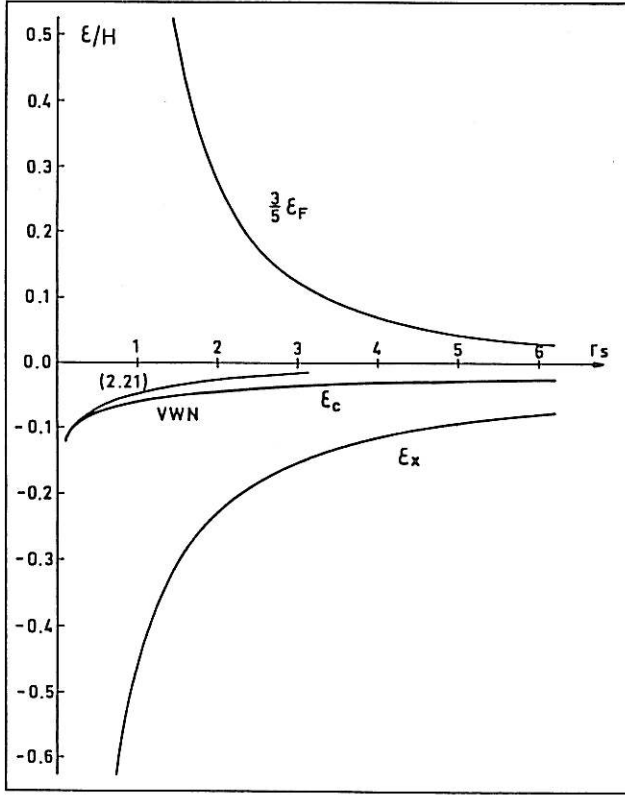


Fig. 2.1. The exchange (ϵ_x) and correlation (ϵ_c) energies per electron in a homogeneous electron gas as a function of the density parameter r_s . The correlation energy is given according to the interpolation formula of Vosko, Wilk and Nusair (VWN) [35], and according to the high density formula of Eq. (2.21). The kinetic energy per electron $\frac{3}{5}\epsilon_F$ is also shown. (1 H = 27.2116 eV)

Next we consider the inhomogeneous electron gas and define the Local-Density Approximation (LDA) as follows. In each volume element of space we use the local electron density and the above relations for the homogeneous electron gas. Thus, we write

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r} \quad (2.24)$$

for the exchange-correlation energy of the inhomogeneous electron gas, where $\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho)$. Using the relation (2.16) we write

$$v_{xc}(\mathbf{r}) = \frac{\delta}{\delta \rho(\mathbf{r})} (\rho \epsilon_{xc}[\rho]) \quad (2.25)$$

for the corresponding exchange-correlation potential, that we apply also locally in space.

We want to emphasize that the LDA, so defined, is an unambiguous approximation that does not contain any adjustable parameters, as is often misunderstood. Though neglecting the long range effects of density variations, the LDA has shown unexpected

successful applicability to electron systems from free atoms to solid matter with a tolerable accuracy of results and correct description of physics and chemistry; as seen in this work and numerous other applications in this field ^[1-5]. Research is going on in order to improve the computational tools by including non-local effects ^[1-3,26,27].

Finally, we introduce the $X\alpha$ approximation, which is widely used in molecular and solid state calculations (see paper VII and the references therein). It originates from Slater's suggestion to approximate the non-local HF exchange potential by its statistical average and the consequent local potential ^[24]. Using the notations above, the $X\alpha$ "exchange-correlation" energy and potential are written

$$\epsilon_{X\alpha}(\mathbf{r}) = \frac{3}{2}\alpha \epsilon_x(\rho(\mathbf{r})) \quad (2.26)$$

and

$$v_{X\alpha}(\mathbf{r}) = \frac{3}{2}\alpha v_x(\rho(\mathbf{r})), \quad (2.27)$$

where α is a parameter, which is usually chosen to equal 0.7. When comparing (2.27) to (2.23), we see that the choice $\alpha = 0.7$ corresponds to $\beta = 1.05$, which is probably suitable, on the average, for the electron densities in atoms and molecules.

3. MODELS AND NUMERICAL METHODS

3.1. Numerical approaches to the Schrödinger equation

Symmetry and asymptotic considerations of the Schrödinger equation and its solutions give qualitative information on the stationary states, allowed transitions and other dynamical properties of the system. However, to obtain quantitative results we are forced to solve the Schrödinger equation explicitly, usually involving physical approximations and numerical approaches.

The numerical electronic structure calculations were initialized and developed together with the quantum theory, first for free atoms and gradually for systems of increasing complexity [1-3,13,38]. Since then, computational physics has shown its power and importance in this field, supporting the theoretical and experimental physics and also having its independent role, as described in an article of Heine [39].

The one-electron Schrödinger equation is a second order differential equation and two types of approaches have been used for its numerical solution. One is a method of direct numerical integration [10,12-15,40,I-III], and the other employs basis functions to expand the one-electron orbitals [5,9,41-43,IV-VII]. It is interesting to note that these two basic approaches to solve the Schrödinger equation are related to the two different approaches of quantum theory, namely the wave mechanics and the matrix mechanics. The Finite Element Method (FEM) for solving differential equations has also recently been introduced into the electronic structure calculations [44] with promising results, which may guide the development of numerical methods in the future.

The methods of direct integration are straightforward. The wave functions, charge densities and potentials are given as their magnitudes in a grid in space, and finite differences in some form are applied to integrate the differential equation point by point in space. The relevant boundary conditions of the wave functions are applied explicitly, as the eigenvalues corresponding to the well-behaving wave functions are searched by fitting the solutions to the boundary conditions.

The use of basis functions usually implicitly includes a great deal of boundary conditions, symmetry properties and other desired features of the solution. These methods may be further classified according to the nature of basis functions and consequent numerics. The basis function representation of wave functions leads to a matrix equation, equivalent with the original Schrödinger equation, and subsequently to solutions in terms of eigenvectors and eigenvalues.

The atom-in-jellium-vacancy model, which we use for solid metals is based on the direct integration of the Schrödinger equation, whereas the cluster model employs basis functions and matrices. Both of these models can be used for free atoms and

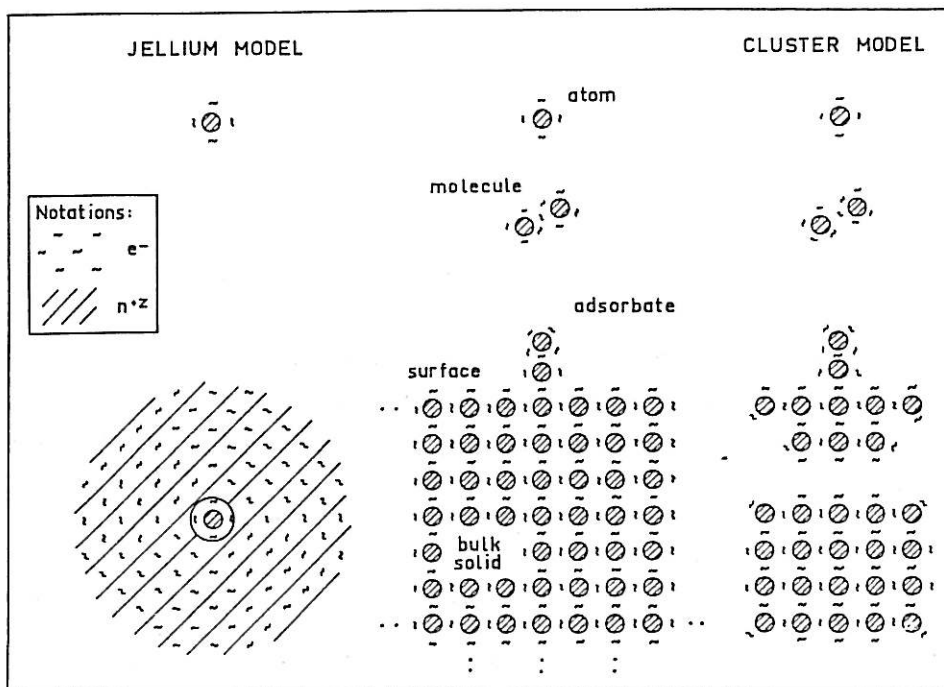


Fig. 3.1. A schematic view of the use of the jellium model and the cluster model.

solids but emphasizing different physical features of the object. An illustration of this is given in Fig. 3.1.

3.2. Atom-in-jellium-vacancy model

In the jellium model of metals the positive charge of ion cores is smeared to a rigid and constant background charge, which assumes the average density of conduction electrons. A spherical vacancy is made in the background and an ion with point nucleus and core electrons is placed at the center of it that retains the charge neutrality. This is the atom-in-jellium-vacancy model^[45], which is illustrated one-dimensionally in Fig. 3.2. This model is spherically symmetric, which simplifies both the concepts involved and the numerical solution of the electronic structure.

Direct numerical integration is usually chosen for systems of high symmetry, in which case the integration grid becomes reasonably small and the boundary conditions become simple. The free atoms, for example, are treated usually with finite difference methods. Spherical symmetry allows us to separate the one-electron equation (2.11) as

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + v_{eff}(r) + \frac{l(l+1)}{2r^2} \right) u_l(r) = \epsilon_l u_l(r), \quad (3.1)$$

and

$$\nabla^2 Y_l^m(\vec{r}) = l(l+1) Y_l^m(\vec{r}), \quad (3.2)$$

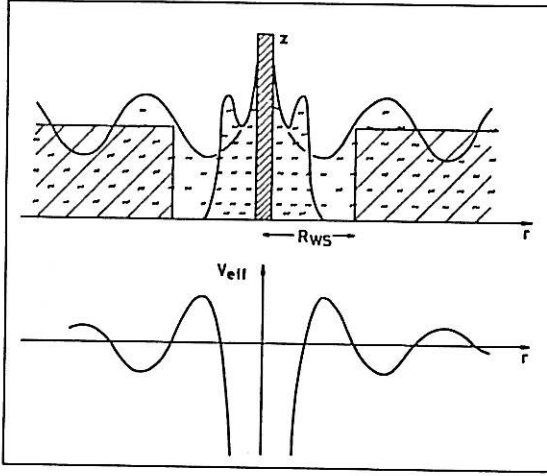


Fig. 3.2. A schematic view in one dimension of the atom-in-jellium-vacancy model and the corresponding one-electron effective potential v_{eff} . The Wigner-Seitz radius (R_{WS}) of the vacancy is marked. For other notations see Fig. 3.1.

with

$$\psi_i^m(\mathbf{r}) = \frac{u_i(r)}{r} Y_l^m(\hat{r}), \quad (3.3)$$

where $\mathbf{r} = (r, \hat{r})$. The level index i stands for the principal and angular momentum quantum numbers, $i = (n, l)$, for bound core levels, but for continuum levels (conduction electrons) the "wave vector" k replaces n , and $i = (k, l)$. The spin is ignored here for simplicity.

The boundary conditions for all one-electron wave functions at the origin are

$$u_i(r) \xrightarrow{r \rightarrow 0} \begin{cases} r - Zr^2, & \text{if } l = 0; \\ r^{l+1}, & \text{if } l > 0, \end{cases} \quad (3.4)$$

where Z is the nuclear charge. At infinity the boundary conditions are different for core and conduction electrons. The core functions vanish exponentially as

$$u_i(r) \xrightarrow{r \rightarrow \infty} e^{-\sqrt{2\varepsilon_i}r}, \quad (3.5)$$

the relation which is used to find the eigenvalues ε_i . The spherical continuum or "scattering" levels behave asymptotically as

$$u_i(r) \xrightarrow{r \rightarrow \infty} r j_l(kr + \delta_i), \quad (3.6)$$

where j_l are spherical Bessel functions and δ_i are phase shifts.

We use the simple free electron energy

$$\varepsilon_i = \frac{1}{2} k^2 \quad (3.7)$$

for all wave vectors and integrate the differential equation (3.1) for a large number of k values, using a one-dimensional grid in the reciprocal space, too. Hence, the

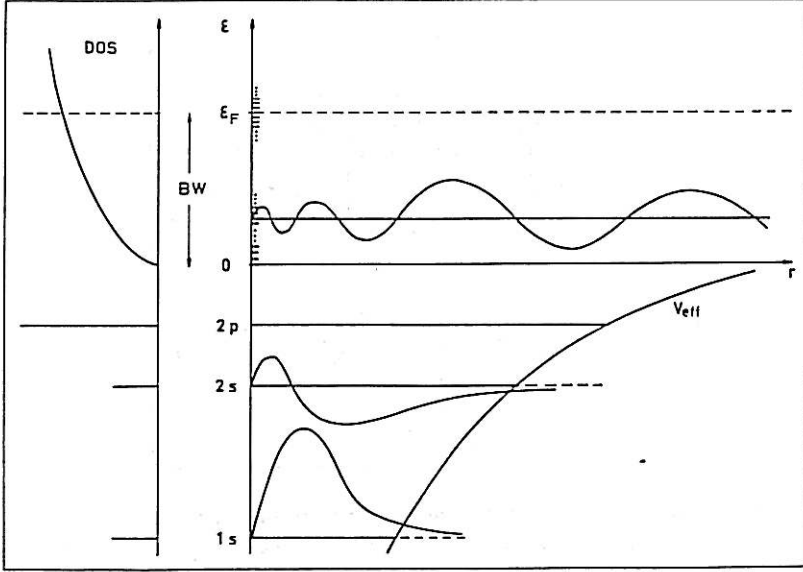


Fig. 3.3. A schematic view of the electronic structure described by the atom-in-jellium-vacancy model. The Fermi level (ϵ_F) and the band width (BW) are denoted.

conduction electrons do not form an eigenvalue problem in this model. The resulting electronic levels of the whole system are schematically illustrated in Fig. 3.3. For a more detailed description of the method refer to ref. 46.

The solutions give the one-electron spectrum and the density of states (DOS), charge density, total energy and all properties derivable from those. Furthermore, both spins are usually treated separately, which allows evaluation of the spin density and magnetic properties. Free atoms can be treated by setting the background density to zero, and hence, comparisons between phenomena in free and metal atoms can be easily performed.

3.3. LCAO cluster model

As shown in Fig. 3.1, clusters can be flexibly used to model the structure of matter from free atoms to solids. A cluster is built by placing the nuclei in space and solving the equations (2.10) - (2.16) for the electronic structure. Starting from free atom one-electron orbitals, such as (3.3) for example, the radial parts can be written as

$$u_{nl}^q(r) = \frac{u_l(r)}{r} \quad (3.8)$$

to be used as atomic basis functions. Free ion orbitals are used as well and the superscript q stands for the ionicity. The symmetry properties of the cluster may be benefited in the numerical procedure and therefore we form the symmetry adapted basis functions

$$\chi_j(r) = \sum_{\nu q n l m} W_{nlm}^{j\nu} u_{nl}^q(r_\nu) Y_l^m(\hat{r}_\nu), \quad (3.9)$$

where $r_\nu = (r_\nu, \hat{r}_\nu)$ is the radius vector relative to the nucleus ν and the coefficients $W_{nlm}^{j\nu}$ are obtained from the group theory. Finally, the one-electron orbitals are expanded as

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) c_{ij} \quad (3.10)$$

using eigenvectors $c_i = \{c_{ij}\}$, which remain to be solved. Thus, the one-electron orbitals are Linear Combinations of Atomic Orbitals (LCAO), which is used as a name for the method.

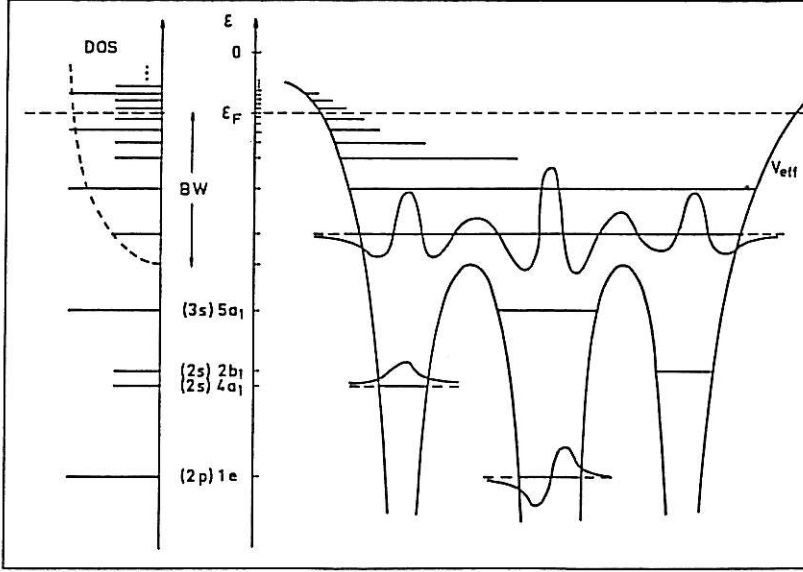


Fig. 3.4. A schematic view of the electronic structure described by the cluster model. The Fermi level (ϵ_F) and the band width (BW) are denoted.

The one-electron Schrödinger equation (2.11) is now written in an equivalent matrix form

$$Hc_i = \epsilon_i S c_i, \quad (3.11)$$

where the matrix elements of the hamiltonian and overlap matrices are

$$H_{kl} = \int \chi_k^*(\mathbf{r}) h(\mathbf{r}) \chi_l(\mathbf{r}) d\mathbf{r} = \langle k | h | l \rangle. \quad (3.12)$$

and

$$S_{kl} = \int \chi_k^*(\mathbf{r}) \chi_l(\mathbf{r}) d\mathbf{r} = \langle k | l \rangle \quad (3.13)$$

The matrix elements vanish unless the basis functions belong to the same irreducible representation of the relevant point group. This leads to a block diagonalization of the matrices in equation (3.11), which simplifies the numerical procedure and allows the classification of solutions according to the symmetry.

The integrals (3.12) and (3.13) are evaluated by applying the Discrete Variational Method (DVM) ^[41], and the matrix equation (3.11) is solved numerically for the

eigenvalues ϵ_i and the eigenvectors c_i , by determining the corresponding one-electron wavefunctions (3.10). The resulting electronic structure is schematically illustrated in Fig. 3.4. For a more detailed description of the method refer to paper VII.

The one-electron spectrum estimates the DOS for both core and valence levels, the charge density and the spin density are obtained from spin-polarized calculations, and the total energy is now available after the last extension [VII]. Generally, the one-electron properties are described fairly well and the total energy evaluation is successfully applied to diatomic molecules [VII]. For larger systems the total energy evaluation using DVM is not, however, so straightforward and should be done with care.

4. APPLICATIONS

4.1. Core level transitions in metal atoms

4.1.1. Screening

The delocalized conduction electrons of metals have a continuous one-electron spectrum across the Fermi level, which allows their easy reorganization with minor costs in energy. Therefore, they are relatively free to respond to perturbations in bulk metal. Core holes in atoms, impurities, vacancies and other defects are efficiently screened, and the long range effects appear only in the form of rapidly decaying Friedel oscillations. These phenomena are well described by the electron gas of the jellium model and the response to the core holes, in particular, is properly reproduced by the atom-in-jellium-vacancy model.

The electron gas response to the (spherical) core hole potential is given by the phase shifts $\delta_L(\epsilon)$, Eq. (3.6), of one-electron wave functions (partial waves) $\psi_{kL}(r)$, where $L = (l, m_l, m_s)$ [48]. Generally, the physical nature and strength of the perturbing potential are given by the generalized partial-wave phase shifts. Fermi level partial-wave phase shifts yield the partial screening charges, which in total contribute to

$$Z = \sum_L \frac{\delta_L(\epsilon_F)}{\pi}. \quad (4.1)$$

The Friedel sum rule states that the screening charge (4.1) is equal to the charge of the perturbation and thus leads to the charge balance [49].

We have carried out spin-polarized calculations for *Li*, *Be*, *Na*, *Mg*, *Al* and *Ca* metals, where the adiabatic partial-wave phase shifts were evaluated for ground states and some core hole states. The metals *Na*, *Mg* and *Ca* were also treated in certain double hole states, which we use to describe the final states of Auger transitions. Our calculated results for the screening of core holes in three different types of metals are shown in Fig. 4.1, both in energy and in space. Only the changes in DOS and in charge density following the ionization are shown. In space, the contributions from other core electrons and conduction electrons to the total response are shown separately. *Li* and *Ca* metals show quite different behaviour compared to *Mg* (or *Na* and *Al*) in the localization of the screening and spin structure, which we use to explain the experimental observations below.

4.1.2. X-ray-edge exponents

Let us consider an x-ray absorption and the consequent core level transition to the unoccupied conduction band. The absorption (or emission) spectrum should appear as

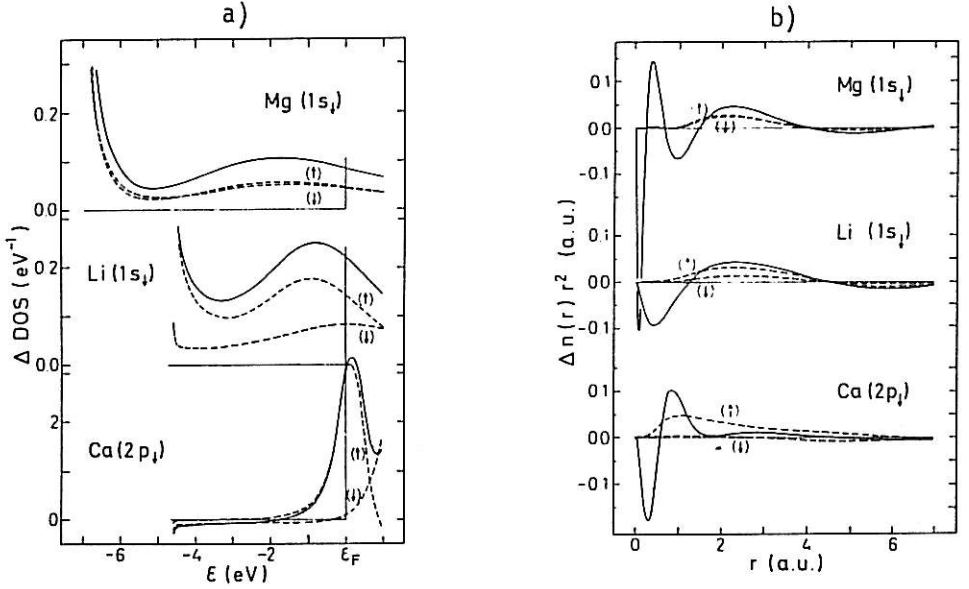


Fig. 4.1. The screening of core holes in *Mg*, *Li* and *Ca* metals. The changes due to the presence of the core hole are displayed a) in the local density of states (DOS), and b) in the radial charge density $n(r)$ (including the core hole in solid lines) [1]. Dashed lines show the spin contributions separately.

a convolution of the core level shape and the band density of states, where the Fermi level appears as an edge. The nature of the core hole potential with the relevant selection rules of the transition may lead either to an increase or a decrease of the transition intensity at the edge, resulting from the dynamic reorganization of electrons at the Fermi level during the transition [46,50–51]. This is seen as sharpening or rounding of the edge in the spectrum and given in terms of edge exponents α_L [52]. The transition intensity near the edge is

$$I(\epsilon) = \sum_L A_L(\epsilon) \left(\frac{\epsilon_c}{\epsilon - \epsilon_T} \right)^{\alpha_L} \Theta(\epsilon - \epsilon_T), \quad (4.2)$$

where the factors A_L are one-particle transition amplitudes, ϵ_T is the edge energy, ϵ_c is some "cut-off" energy and $\Theta(\epsilon)$ is a step function. Due to the selection rules included in A_L , only one of the l channels usually contributes which leads to the intensity distribution $\epsilon^{-\alpha_l}$ at the edge.

The adiabatic Fermi level partial wave phase shifts $\delta_L(\epsilon_F)$ can be used to evaluate the strength of this dynamic many-body process and the exponent [50–52] is

$$\alpha_L = \frac{2\delta_L(\epsilon_F)}{\pi} - \alpha, \quad (4.3)$$

where

$$\alpha = \sum_L \left(\frac{\delta_L(\epsilon_F)}{\pi} \right)^2. \quad (4.4)$$

Thus, there exist two contributions in the edge exponent (4.3): the first one resulting from the change in the transition probability due to the screening and the other one (4.4) resulting from the reorganization of other electrons at the Fermi level.

The x-ray edge exponents for *Na*, *Mg* and *Al* are well established both theoretically and experimentally [53], and our calculations are in good agreement with those results. But for *Li*, *Be* and *Ca* neither the experimental situation nor the theoretical results are yet established. A broad K edge of *Li* has been observed and various explanations have been suggested [53]. Girvin and Hopfield first suggested that the spin or the exchange effects may play an important role in the screening of a *Li* core hole [54], which is our result, too. We find a strongly spin-polarised screening of a *Li* 1s hole, as seen in Fig. 4.1, leading to a negative α_1 ($l = 1$) explaining, at least partly, the broad K edge. We want to emphasize that our negative α_1 results from the spin-polarisation effect, whereas some other theoretical results lead to a negative α_1 only as a compensation of much larger s ($l = 0$) screening, i.e. a much larger α_0 [1]. Unfortunately α_0 is not experimentally measurable, because the L edge of *Li* metal does not exist.

4.1.3. Asymmetric line shapes

In the core level ionization or Auger transition the conduction electrons are not directly involved but only perturbed by a sudden creation of the core hole potential. Again the dynamic response of conduction electrons can be given in terms of adiabatic partial-wave phase shifts, and the total "strength" is given by the quantity α in Eq. (4.4), in a spherically symmetric approximation [52]. Using the concepts of a one-electron picture, the perturbation of a suddenly created core hole induces an infinite number of infinitely small excitations at the Fermi level, called electron-hole pairs. The energy spectrum of these excitations appears to be singular at zero energy and therefore the number α , defining the strength of the singularity, is called the singularity index.

In the experimental kinetic energy spectrum of emitted electrons the energy loss is seen as a low energy tail of the primary peak. The resulting asymmetric Doniach-Šunjić line shape [55] is a convolution of the natural line shape and the singular energy loss spectrum. The larger the singularity index α is, the stronger the asymmetry appears in the line shape.

The singularity indices for *Na*, *Mg* and *Al* are small and well established but for the other metals considered the spin-polarised screening plays a significant role in the resulting line shapes. The fully spin-polarized screening of the core hole in *Ca*, see Fig. 4.1, increases the singularity index to more than double the corresponding spin-symmetric value, see paper I, thereby predicting extremely asymmetric XPS lines ($\alpha = 0.35$). The exceptionally strong screening of the *Ca* core hole is explained by the unoccupied d shell of the ground state, which then becomes occupied by a localized screening charge, if a core hole is present. The screening charge, albeit being in the conduction band, shows a shape and localized structure in energy that is very similar to that of a bound 3d electron.

The Auger line shapes for the studied *Na*, *Mg* and *Ca* metals were found to be the same as the XPS line shapes with singularity indices of 0.14, 0.11 and 0.35, respectively. Our experimental Auger lines of *Ca* show the predicted extremely asymmetric shape

leading to the anomalous spectrum, which is discussed in paper II. The localized screening may also be behind the observed sharpness of valence Auger lines.

4.1.4. Solid state shifts

The difference between the initial and final state energies of the transition gives the transition energy, i.e. photoelectron energy E_{XPS} or binding energy E_B and Auger electron kinetic energy E_A . Performing the corresponding calculations for both solid metal and free atoms we can compare the solid state effects on the transition energy. The solid state shifts, or extra-atomic relaxation energies, are defined as

$$\Delta E_{XPS} = E_B^a - E_B^s - \Phi \quad (4.5)$$

and

$$\Delta E_A = E_A^s - E_A^a - \Phi, \quad (4.6)$$

where the superscripts *a* and *s* refer to the free atom and solid state, respectively. The work function Φ is the difference between the vacuum and Fermi levels, which are the experimental reference levels of free atom and solid state transition energies, respectively.

Table 4.1. Calculated solid state shifts for photoelectron energies (Eq. (4.5)) and Auger electron energies (Eq. (4.6)), and a comparison with the experimental data [I,II]. (All values are in eV).

	Calculated	Experimental
Li 1s	7.0	
Be 1s	8.0	
Na 1s	5.4	4.9
2s,2p	5.3	
KLL	15.2	14.3
Mg 1s	5.1	4.9
2s,2p	4.8	
KLL	15.6	15.0
Al 1s	6.2	6.3
2s,2p	5.7	
Ca 2p	9.4	8.3
3p	8.0	6.1
LMM	19.9	20.3

The evaluated solid state shifts are given in Table 4.1, and are seen to be in good agreement with the experiments, where experimental values are available. For *Li* and *Be*, the shifts are large but unfortunately, to our knowledge, there is no experimental data to compare with. For the double hole final state of *Ca* we have two possible spin arrangements, opposite and parallel, which may be used to estimate the extent of multiplet splitting. Our calculations predict for the solid state spectrum a splitting of

roughly twice the atomic one, which is the experimental result, too ^[11]. In conclusion, the atom-in-jellium-vacancy model was shown to be better in predicting the solid state shifts in metals compared to the other theoretical methods available ^[1].

4.2. Charge density and form factors of the *Al* metal

The use of the spherical atom-in-jellium-vacancy model raises a question, namely to what extent a spherical description of the crystal potential and charge density is justified. The reason is the conduction electrons, which fill the interstitial region between the nearly spherical ion cores. They feel the periodic lattice structure of the metal crystal and may contribute to oriented bonding between the metal atoms resulting in non-spherical contributions. We have studied this question together with the evaluation of atomic form factors for the *Al* metal within the atom-in-jellium-vacancy model through a comparison with experiments and other theoretical results.

The atomic form factor, defined as a Fourier transform of the (atomic) charge density $\rho(\mathbf{r})$,

$$f(\mathbf{G}) = \int \rho(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}} d\mathbf{r} \quad (4.7)$$

expresses the wavelengths of the density oscillations and is a measure of centralization of the charge distribution. Using the atom-in-jellium-vacancy model we have evaluated the contributions from core and conduction electrons separately for *Al* and found an agreement with the experiments within the experimental uncertainty ^[11]. Unfortunately, the conduction electron contribution is of the same order of magnitude with the experimental uncertainty and therefore the comparison does not answer the question we posed for the spherical model. Therefore, we compare the valence contribution to the form factor (4.7) with other theoretical results from methods, where the full three dimensional lattice structure is taken into account. This is done in Fig. 4.2, where we can see that the atom-in-jellium-vacancy results closely follow the other theoretical results.

Perrot ^[56] argued that the non-spherical part of the valence density of *Al* is essential and contributes too much to be ignored. His method of calculation is based on the Muffin-Tin (MT) approximation with a multipole expansion and his results are in good agreement both with experiments and with other theoretical methods. However, our results are surprisingly similar to the Perrot's LDA results, see Fig. 4.2. This leads us to the opposite conclusion that the spherical atom-in-jellium vacancy valence charge density is quite adequate, at least for the evaluation of form factors. We note, however, that Perrot's different definition of the spherical charge based on the MT approximation may be the origin of this discrepancy.

Attempts to include the crystal lattice effects in the jellium model, still retaining the spherical symmetry, has been done using the so called Spherical-Solid Model (SSM) ^[58,59]. In SSM pseudopotentials are used to form the three dimensional potential of the crystal, which is then spherically averaged to a spherical-solid potential. It is then added as a correction to the spherical one-electron effective potential, such as the atom-in-jellium-vacancy potential, for example. We have made a new and simpler approach to SSM and replaced the pseudopotential by the atom-in-jellium-vacancy potential itself, and furthermore, allowed the sum of the atom-in-jellium-vacancy potential and the spherical-solid potential to become self-consistent. This model, which we call a

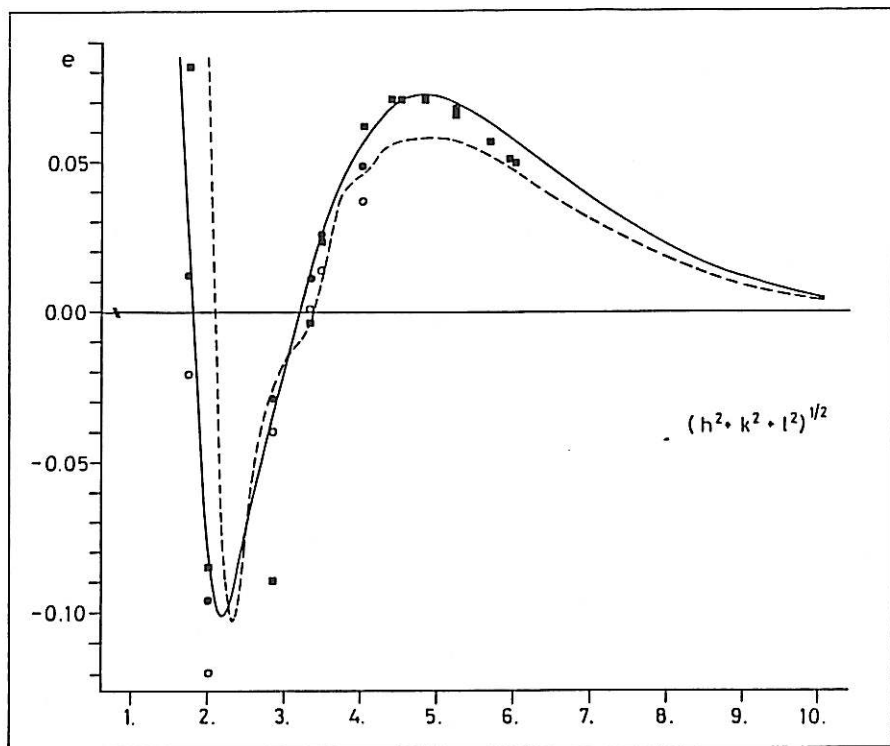


Fig. 4.2. The conduction electron contribution to the atomic form factors of Al, from the atom-in-jellium-vacancy model (solid curve) and from the SCF-SSM (dashed curve), see text. Perrot's LDA results (filled circles) and APW-HF results (open circles) are also shown [56]. Other calculated results (filled quadrangles) are from ref. 57.

Self-Consistent SSM (SCF-SSM), was used to examine the crystal structure effects on the electron density and form factors.

We found that the lattice structure does not play an essential role but its inclusion in a spherically averaged way leads to an improvement of form factors for large wave vectors, i.e. short wavelength oscillations, see Fig. 4.2. However, the contributions from the long wavelength oscillations seem to impair the form factors leading us to conclude that other than the nearest neighbours are not properly described within this model.

4.3. Chemical reactivity

Chemical reactions progress under the laws of thermodynamics. Looking at the microscopic level, however, the reactions are driven by forces between the involved components, and their reaction paths with minima and activation barriers are better understood using molecular and atomic concepts. Therefore, a detailed knowledge of the reaction mechanisms is not only of fundamental but also of great practical interest [60], giving help in tracing the rate limiting steps, their removing and in designing of

industrial reactions using catalysts with desired activity and selectivity. This may lead to such concrete goals, as improvement of the quality of products, decrement of pollution problems and minimization of energy costs.

4.3.1. Catalysis

Catalysts are used to speed up otherwise slow reactions. They are those components of the reaction, which are not consumed but only lower the critical activation barriers or even open up new reaction paths with higher reaction rates. One distinguishes between two types of catalysis, homogenous and heterogeneous. Here we will consider only the heterogeneous catalysis, which involves the reactants and the catalyst in different phases. Such examples are pure metals or metal compounds, either in the form of small particles or as solid surfaces. A typical surface catalyzed reaction proceeds via adsorption of the reactants on the surface, diffusion of the adsorbates on the surface, the reactions, and finally the desorption of the reaction products. It is interesting to note how seemingly small changes at the surface; the choice of substrate, alloying, surface plane, surface defects, coadsorbates, etc., may have dramatic effects on the catalytic activity.

The driving forces and the reaction path at the microscopic level can be derived from the potential energy (hyper)surfaces (PES), by which we mean the total energy of the system as a function of the space coordinates of all relevant atoms involved. The potential energy curve of a diatomic molecule is a one-dimensional PES and equipotential (total energy) contours of a single adsorbate as a function of distances from and along the surface illustrates a two (or three) dimensional PES. As an example, the PES for a hydrogen atom on a $Ni(111)$ surface is shown in Fig. 4.3. Generally, the potential energy hypersurface is a $3N-5$ dimensional function for N participating atoms but in practice only a few of the coordinates need to be considered independently.

A potential energy surface for a reaction gives a comprehensive picture of the whole reaction mechanism, and in particular, the reaction path and the minimum barriers, which are the activation energies. Intermediate physisorption and chemisorption or precursor states of the reaction are seen as minima at the PES, the depths of which give the corresponding physisorption and chemisorption energies. Locations of the minima at the PES give the bond lengths, adsorption sites and equilibrium geometries. And finally, curvature of the minima yield the vibrational frequencies, and generally, the shape of the PES determines the whole adiabatic dynamics of the process.

The various degrees of freedom of the adsorbate/substrate energy can be roughly classified into the translational, chemical and internal forms, and substrate excitations. Energy exchange processes between these forms of energy are the other key quantities in describing the reaction dynamics and catalysis. For surface reactions the kinetic energy loss of an impinging reactant particle and the energy conversion to the kinetic energy of a desorbing product particle are the most important energy exchange processes. The kinetic energy loss during the adsorption is usually due to the internal excitations or the dissipation to the substrate excitations, such as electron-hole pairs or phonons. And inversely, for desorption the internal excitations or the phonons are the sources of escape energy for the product particle.

Different PES can also be assigned to different excitation levels of some particular

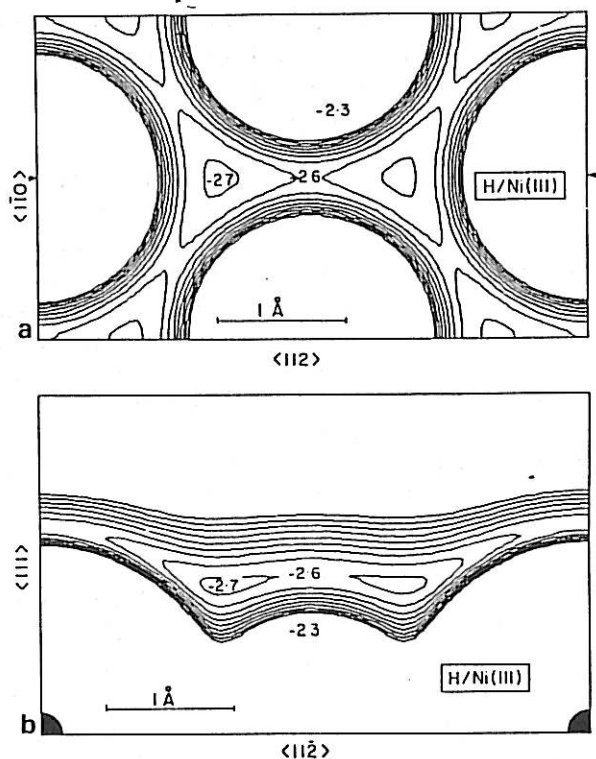


Fig. 4.3. Contours of constant potential energy (PES in steps of 0.05 eV) for a hydrogen atom on a Ni(111) surface, along cuts through minimum energy points a) parallel to the surface and b) perpendicular to the surface ^[61].

degree of freedom in energy. This is the case, e.g. when going from the classical vibration on a single PES to the quantum mechanical description, and when assigning different (diabatic) PES for different excited electronic states. Such a picture allows the energy exchange to be described as transitions between the different PES.

The picture of potential energy surfaces and energy exchange processes has been shown to be successful in explaining the reaction mechanisms and the roles of various factors affecting the reaction rates and cross-sections, equilibrium states and configurations, etc. Sufficient knowledge of this kind, combined with statistical mechanics or thermodynamics gives the whole reaction dynamics and even makes dynamical computer simulations feasible for systems, which are otherwise too complicated to handle.

4.3.2. One-electron properties

For evaluation of a PES, the laborious total energy calculation must be repeated a number of times. However, without direct access to a theoretical PES a great deal of useful knowledge about reactivity is obtainable from the one-electron properties. The Fermi level electronic structure, in particular, for the case of metal substrates explains the essential features of adsorption. The adsorption of carbon monoxide (CO) on

transition metals, for example, has been analyzed in terms of charge transfer at the Fermi level to and from the CO molecule [62]. The one-electron structure also explains, to a large extent, such important catalytic phenomena as poisoning, promotion and active sites of substrates [60].

The coadsorbates on the catalyst surface that hinder the reaction are called poisons and those which increase the reaction rate are called promoters. The simplest explanation is that the coadsorbate effects the Local Density Of States (LDOS) at the reactant adsorption site. Similarly the active sites, steps, terraces, adatoms, surface vacancies, dislocations and other surface defects may effect the LDOS. These effects are simply local changes in the electron density and the consequent changes in the potential, or they may include changes in the occupations of levels of different symmetry. The increased LDOS at the adsorption site of a CO molecule, for example, leads to an increased occupation of the antibonding, lowest unoccupied molecular orbital (LUMO) of the molecule and a dissociation may result. The symmetries of the highest occupied molecular orbital (HOMO) and LUMO and their matching to the LDOS of the adsorption site also play a significant role in the hybridization and chemical bonding or in dissociation.

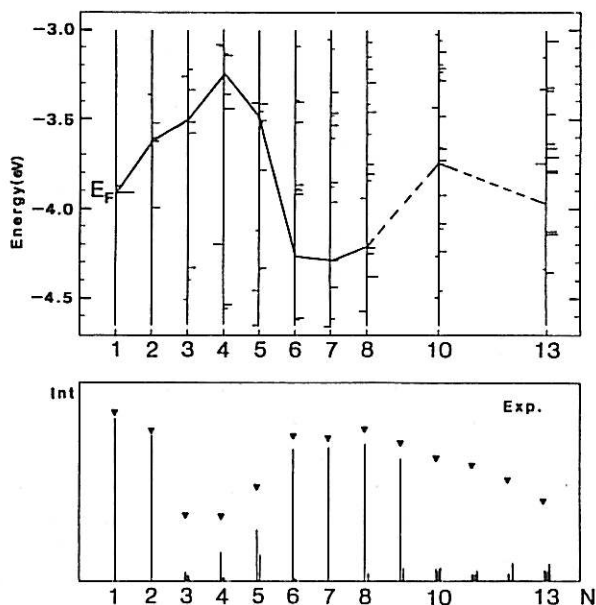


Fig. 4.4. One-electron levels and the "Fermi level" of Co clusters (upper panel) calculated with the bond length of the Co dimer. The experimental photoionization mass spectra (lower panel) for pure (triangles) and reacted (bars) Co clusters is also shown [63]. The difference between these two experimental spectra shows the reactivity.

We have studied the reactivity of small cobalt (Co) clusters with H_2 molecules

using the one-electron properties and the HOMO/LUMO concepts, and explained the experimentally observed variation in the reactivity as a function of cluster size. It was found experimentally [63] that the activity of H_2 (D_2) adsorption on the Co_N clusters in a supersonic beam depends strongly on the cluster size, see Fig. 4.4. The clusters with $N = 3, 4, 5$ and $N \geq 10$ were very active, while clusters of other sizes appeared to be quite inert. The activity of H_2 adsorption on transition metals is a general trend [61,64] but the observed exceptional cluster size dependence deserves to be studied. A similar behaviour was observed for the Fe_N clusters and a correlation with the cluster ionization energy was found [65]. The question is, whether similar reasons are behind the varying activity of Co_N clusters.

We have evaluated the spin-polarized electronic structures of Co_N clusters, with $N = 1 - 8, 10, 13$ using simple geometries of C_{3v} symmetry and a principle of maximum bonds between atoms. The two extreme values of the bond lengths obtained from the dimer and the bulk cobalt were used. A double basis with virtual atomic and ionic functions was employed, and a Fermi-Dirac distribution with $T = 160K$ for the occupation of the levels was used.

From the results, shown in Fig. 4.4, we first notice the variation of the "Fermi level" as a function of cluster size, and the correlation between the lower ionization energy and the observed reactivity. Secondly, we note that the difference between the HOMO and LUMO is much smaller in the active clusters, leading to easier reorganization of electrons at the Fermi level; a property which is typical for solid metals. Further observations on exchange splitting, symmetry characters of HOMO and LUMO levels, atomic orbital populations in the cluster, different behaviour of majority and minority spin levels, and the magnetic moments versus cluster size can be done and correlations with the reactivity are found [17]. However, to reveal their specific roles, the electronic structures of the combined system of H_2 and Co_N should be examined.

4.3.3. Electronic damping of adsorbate motion

As pointed out above, the energy exchange processes are important, and the kinetic energy loss of a reactant particle impinging on a surface, in particular, plays an essential role in adsorption and surface reactions. The kinetic energy of an adsorbate can be either transferred to the internal degrees of freedom of the adsorbate or dissipated into the substrate. Here we consider the dissipation channel to the substrate excitations in the form of electron-hole (e-h) pairs. The relative importance of the e-h pairs in the dissipation depends on the nature of the substrate and adsorbate; the e-h pair channel being most important for reactive adsorbates on metal surfaces. The motion of a reactive adsorbate has large effects on the electronic structure at the Fermi level, which implies the excitation of the e-h pairs.

As a model for the energy dissipation from the adsorbate motion we have studied the damping of CO vibrations on a $Cu(100)$ surface. This is experimentally well known and shown to originate from the e-h pair creation [66]. The damping of the CO stretch vibration is very effective and it is seen experimentally as an extremely short lifetime of vibrational excitations resulting in a ten orders of magnitude larger line width, compared to that of a free molecule. The experimental result for the line width is $\Gamma = 0.5$ meV [66].

We have used a finite cluster approach to evaluate the electronic structure of the CO molecule adsorbed on the Cu(100) surface (CO/Cu₉(100)). The cluster allows a proper description of the adsorption site, bonding between the adsorbate and substrate and bonding between the substrate atoms, in contrast with the jellium surface model. The cluster being just a large non-relaxed molecule also allows us to use all the methods and concepts available for molecules. Furthermore, one can expect the localized substrate response to the adsorbate vibration to be reasonably described in a finite cluster substrate. In our case, however, although the phenomenon considered obviously is very localized, the e-h pairs must be described in terms of delocalized conduction electrons at the Fermi level. Therefore, the quasi-continuous one-electron spectrum of conduction electrons must be added to the finite cluster model.

We have examined a simple solution to this problem and shown that broadening of the discrete one-electron levels leads to a proper model for the continuous DOS at the Fermi level. In Fig. 4.5. the continuous density of states relevant to our case is shown for the cluster CO/Cu₉(100). It is in a good agreement with a photoemission experiment [67]. The broadening of the levels may be understood to describe embedding of the cluster onto an infinite substrate and the consequent coupling (hybridization) to the substrate electrons.

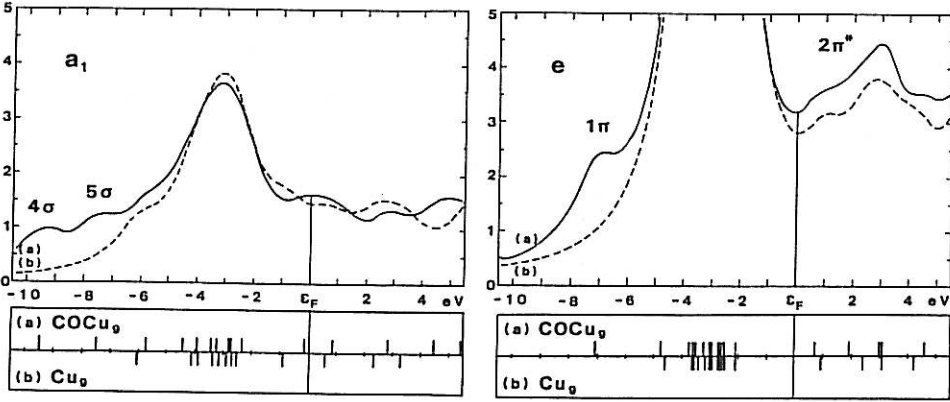


Fig. 4.5. One-electron levels (lower panels) of the symmetries a_1 and e and the resulting "continuous" density of states (upper panels). Both the bare substrate Cu₉ (dashed curve) and the cluster CO/Cu₉ (solid curve) results are shown [67].

In describing the dynamical rate of creating e-h pairs we use the adiabatic concepts again, in analogy with section 4.1.3. The strength of the perturbing potential of the vibrating molecule may be given in terms of the adiabatic charge transfer between allowed channels, or formally, changes in generalized scattering phase shifts of one-electron partial waves [68]. It is convenient to express the energy transfer from vibrational excitations to the e-h pairs in terms of the vibrational line width as

$$\Gamma_q = \frac{\pi \hbar^2}{M} \sum_L \left(\frac{\partial q_L}{\partial Q} \right)^2 \quad (4.8)$$

in the quasi-static limit and one-electron approximation [69]. We have written Q for the normal coordinate of vibration, M for the reduced mass and q_L for the occupation of the channel $L = (\eta, m_\eta, m_s)$, where η stands for the irreducible representations of the relevant point group, m_η for its degeneracy and m_s for the spin orientation. It should be noted that the charge balance requires that

$$\sum_L \frac{\partial q_L}{\partial Q} = 0 \quad (4.9)$$

in analogy with the Friedel sum rule.

Performing two additional calculations, one with the contracted bond length and one with the stretched bond length of CO , we obtain numerical estimates for the derivatives in Eq. (4.8), which results in $\Gamma_q = 0.5$ meV with an uncertainty of about 0.2 meV. A comparison with the experimental linewidth $\Gamma = 0.5$ meV [66] shows that we can describe the e-h pair excitation process with the calculated data of a finite cluster fairly well, and the suggested [70] picture of the damping mechanism with the "fluctuation" in the occupation of $2\pi^*$ resonance is also ascertained. Furthermore, the picture of CO adsorption on a Cu surface with the σ charge donation and π charge backdonation was verified. The cluster size effects were extensively examined [17] and found to be negligible in the numerical value, which we obtain.

Finally, the present success leads us to suggest that the finite-cluster approach might be applicable to studies of electronic damping of other adsorbate motions, too.

4.4. Potential curves of diatomic molecules

The self-consistent total energy is the most essential quantity which results from electronic structure calculations. But its evaluation is not straightforward — it requires sophisticated methods and skillful use of numerical procedures to achieve a reasonable accuracy with tolerable efforts. Nevertheless, it is needed for the evaluation of electronic transition energies, potential energy surfaces with equilibrium geometries, vibrational properties, dissociation energies, reaction paths, activation and chemisorption energies, etc. Therefore, the LCAO-cluster method used in this work was extended to incorporate the total energy evaluation, and as a first test the potential curves of the diatomic molecules CO and N_2 were calculated.

An accurate evaluation of total energy relies on the accurate self-consistent solution of the Schrödinger equation. It consists of two stages in a loop: solving the one-electron equations in the effective potential, and then, solving the Poisson equation of the charge density for the effective potential. The recent work of Delley and Ellis on improvements for solving the Poisson equation using the Self-Consistent Multipolar (SCM) expansion of the charge density [42] within the DVM-LCAO procedure increased the quality of the self-consistent solution to a level where the total energy evaluation became reasonably accurate [43]. Our procedure for the total energy evaluation is based on the same solution but differs in details from that of Delley *et al.* [17].

The potential energy curves, dissociation energies, bond lengths and vibration frequencies were evaluated for CO and N_2 , for which there exist accurate $X\alpha$ results and experiments to compare with. Therefore, we used the $X\alpha$ approximation, too. The resulting potential energy curves are shown in Fig. 4.6. For other results refer

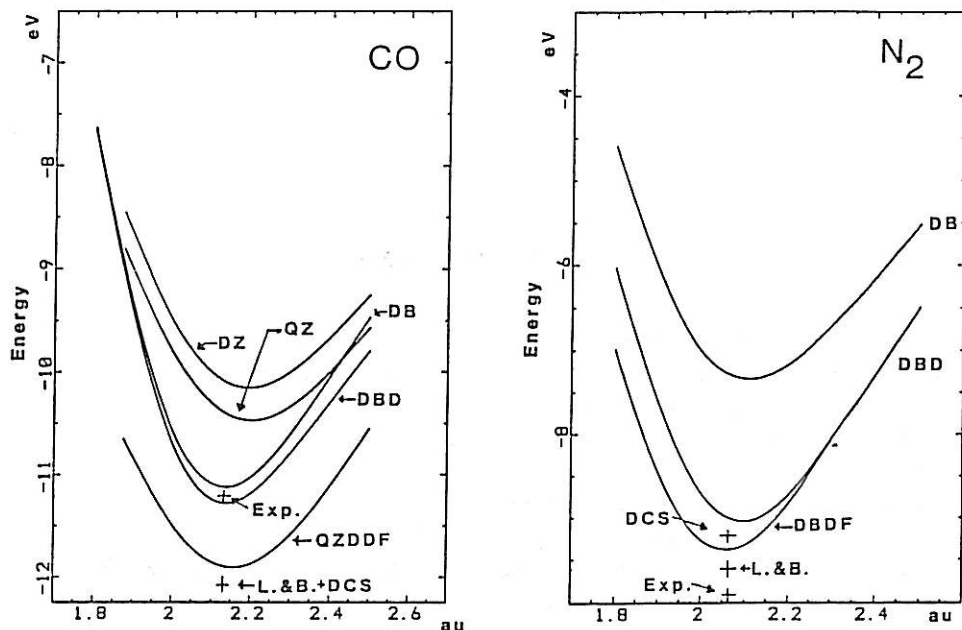


Fig. 4.6. Potential curves for the diatomic molecules CO and N_2 from calculations with the double basis (DB), the additional d functions (DBD), and the additional d and f functions (DBDF). Other calculated results and experimental results (Exp) are also shown (see paper VII for details).

to paper VII. We have found a good general agreement between the experiments and the $X\alpha$ results, as also pointed out before ^[71]. The accuracy of our results appears to be mainly determined by the completeness of the basis set, the quality of the SCM charge density fit and the numerical noise of DVM, and a combined effect of the last two.

We want to remark that our method is a general purpose one, to treat systems of different size and nature, and we do not rely on the choice of a coordinate system or other such details that is often done. Our free atom wave functions, used as numerical basis functions, are in no way optimized, but however, they appear to be rather efficient in the total energy evaluation. Therefore, we expect our method to be efficient also for large and complicated systems.

5. CONCLUSIONS

The electronic structure investigations in this thesis range from applications in spectroscopy [I-III] to problems in chemistry and catalysis [IV-VI]. These have been done using first principles calculation methods based on the local-density approximation to the many-body correlations of electrons. A large part of this work concerns development of physical models for the description of different phenomena [I,III,V,VI] and development of numerical or other calculation methods [III,VII]. A general conclusion is that the local-density approximation is, though simple, computationally effective and makes both qualitative and quantitative calculations feasible for the whole field of applications considered.

The response of conduction electrons to the core level electronic transitions of metal atoms appears to be well described by the atom-in-jellium-vacancy model. The consequent screening effects in terms of the evaluated x-ray edge exponents, singularity indices or asymmetric line shapes and solid state shifts show a good agreement with the experimental electron spectra. Furthermore, the spin-polarisation of the screening was found to be important for *Li* and *Be* metals explaining the experimentally observed broad K-edge of *Li*. For the core ionisation of the *Ca* metal the screening was found to be very localized, atomic 3d-electron-like and entirely spin-polarized, explaining the anomalous Auger spectrum and the large solid state shift.

The spherical atom-in-jellium-vacancy model is a simple and useful description of both the core and conduction electrons of metals. The spherical description of conduction electron distribution was found to be justified, regarding the atomic form factors of the *Al* metal, although opposite arguments have been presented in the literature. A simple spherical-solid model, to include the crystal lattice effects, was used and the idea of self-consistency of the model was introduced. It was applied to the form factors of *Al*, which led to the conclusion that only the description of nearest neighbour interactions was improved.

Chemical reactivity and catalysis can be studied at the atomic level most easily by using the potential energy surfaces (PES) of the reaction constituents. However, even without the theoretical PES, we have been able to explain the varying reactivity of small *Co* clusters in terms of one-electron structure at the Fermi level. We have demonstrated that the ionisation energies together with the symmetries and spin structure of HOMO and LUMO explain the observed, exceptional reactivity dependence on the cluster size.

Energy dissipation from the adsorbate motion to the substrate, which is an important step in surface reactions, is a dynamic process. However, using a cluster model

for a CO molecule adsorbed on the $Cu(100)$ surface we have been able to evaluate the rate of energy transfer from the CO vibration to the electron-hole pair excitations in the substrate in terms of adiabatic screening charges. It requires, however, a model for the quasi-continuous energy spectrum of delocalized conduction electrons that is not inherent in a finite cluster. A good agreement with the experimentally measured data is obtained and the proposed picture of the adsorption and charge transfer processes is verified. The success of our model suggests further applications for it.

Finally, a total energy procedure was implemented to the LCAO cluster code, and as a first test the potential curves of the diatomic molecules CO and N_2 were calculated with satisfactory results. The vibration frequencies, bond lengths and dissociation energies were compared to the results of other, more sophisticated, calculations and experiments, and an agreement was found. The numerical accuracy of the method and the effects of basis set incompleteness was also discussed.

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