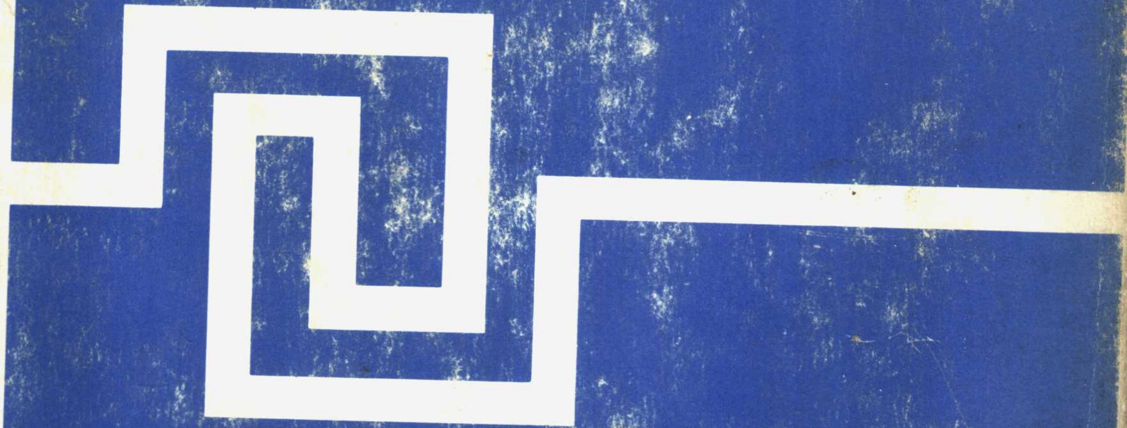
Electrons in Disordered Metals and at Metallic Surfaces

Edited by
P. Phariseau
B.L.Györffy
and
L. Scheire



NATO ADVANCED STUDY INSTITUTES SERIES

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Electrons in Disordered Metals and at Metallic Surfaces

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Preface

We present here the transcripts of lectures and talks which were delivered at the NATO ADVANCED STUDY INSTITUTE "Electrons in Disordered Metals and at Metallic Surfaces" held at the State University of Ghent, Belgium between August 28 and September 9, 1978.

The aim of these lectures was to highlight some of the current progress in our understanding of the degenerate electron 'liquid' in an external field which is neither uniform nor periodic. This theme brought together such topics as the electronic structure at metallic surfaces and in random metallic alloys, liquid metals and metallic glasses. As is the case in connection with infinite ordered crystals, the central issues to be discussed were the nature of the electronic spectra, the stability of the various phases and the occurrence of such phenomena as magnetism and superconductivity.

In the theoretical lectures the emphasis was on detailed realistic calculations based, more or less, on the density functional approach to the problem of the inhomogeneous electron liquid. However, where such calculations were not available, as in the case of magnetism in random alloys and that of metallic glasses, simpler phenomenological models were used.

The theoretical discussions were balanced by reviews of the most promising experimental techniques. Here the stress was on results and their relevance to the fundamental theory. Moreover, the attention had centered on those experiments which probe the electronic structure in the greatest detail.

While the individual contributions are selfcontained accounts of the relevant topics, and no effort has been made to standardize the notations all through the text, cross references are frequent and each is written with evident awareness of the unity of the subject. It is hoped that by bringing together a variety of efforts to deal with the same underlying problem, namely the lack of crystalline symmetry, they would illuminate each other. Furthermore, the juxtaposition was also intended to call attention to the interesting variety of phenomena such broken symmetry can give rise to.

Unfortunately Professor Soven, Dr. Pendry and Dr. Bergmann, whose lectures contributed much to making the summerschool a balanced discussion of the subjects at hand, were unable to prepare their lecture notes for publication. Nevertheless, we have included a short summary of their contributions together with useful lists of suggested readings at the end of this volume (p.553).

The Advanced Study Institute was financially sponsored by the NATO Scientific Affairs Division (Brussels, Belgium). Co-sponsors were the National Science Foundation (Washington, D.C., U.S.A.), the Department of Higher Education and Scientific Research of the Ministry of National Education and Culture (Brussels, Belgium), and the Faculty of Sciences of the State University of Ghent. In particular we are indebted to Dr. T. Kester of the NATO Scientific Affairs Division, Prof. Dr. J. Hoste, President of the University of Ghent and Prof. Dr. R. Mertens, Dean of the Faculty of Sciences.

We are grateful to all lecturers for their most valuable contribution and their collaboration in preparing the manuscripts. Thanks are also due to the members of the International Advisory Board : F. Abelès (Paris, France), S. Berko (Waltham, Mass., U.S.A.), W. Dekeyser (Ghent, Belgium), H. Ehrenreich (Cambridge, Mass., U.S.A.), J.S. Faulkner (Oak Ridge, Tenn., U.S.A.), V. Heine (Cambridge, U.K.), S. Lundqvist (Gothenburg, Sweden) and W. Plummer (Philadelphia, Pa., U.S.A.).

The Institute itself could not have been realized without the enormous enthusiasm of all participants and lecturers and without the untiring efforts of our co-workers Mr. R. Rotthier and Mr. P. Van Steenberge at the "Seminarie voor Theoretische Vaste Stof- en Lage Energie Kernfysica". Also, Mrs. A. Goossens-De Paepe's help in typing the manuscripts is gratefully acknowledged.

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Ghent and Bristol, December 1978

Contents

THE DENSITY FUNCTIONAL THEORY OF METALLIC SURFACES

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1. INTRODUCTION

Most calculations on clean surfaces and surfaces with chemisorbed atoms or molecules can be divided into two classes. In the first, one constructs a model Hamiltonian, for example for chemisorption systems the Anderson model |1| is often used. Usually the model is fairly simple and well suited to give a conceptual understanding of important features of the system as well as an indication of the importance of many-body effects |2|. In the second class one uses the density-functional (DF) formalism |3,4| or the Xα method |5|, which can be considered as a special case of the DF formalism. In this approach, ground-state properties are obtained by solving a Hartree-like equation (Eq. (10) below)

$$\{-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\}\,\psi_\nu(r) = \varepsilon_\nu\,\psi_\nu(r) \qquad (10)$$

The relative simplicity of this equation makes it possible to use a fairly detailed and specific description of the system, without obtaining an unmanageable problem. The crucial quantity in Eq. (10) is $v_{eff}(r)$ which, in principle, contains all many-body effects. As a simple approximation for $v_{eff}(r)$, the so-called local density (LD) approximation, has been found to give generally good results, the method has become very popular. A detailed discussion of the DF formalism and the LD approximation is given in section 2.

The DF formalism has been applied by Lang and Kohn to the so-called planar uniform background model of a surface. They calculated properties such as the charge density, work function and surface energy and obtained good agreement with experiment (in the case of the surface energy the model needed to be refined slightly). Recently, models have been developed which take the atomic structure of the surface more explicitly into account. However, the simpler calculations of Lang and Kohn are still of great importance for our understanding of the surfaces of simple metals, and are described in section 3.

The planar uniform-background model has been used by Lang and Williams and by Gunnarsson, Hjelmberg and Lundqvist to describe chemisorption of atoms on simple metals. In section 4 selected results for H, Li, Si, Cl and Na chemisorbed on Al, Mg and Na are discussed.

2. THE DENSITY FUNCTIONAL FORMALISM

2.1. Basic Theorems

The DF formalism is based on two papers by Hohenberg and Kohn |3| and Kohn and Sham |4|. The basic quantity in this theory is the electron density $n(\underset{\sim}{r})$, and we will first show the relation between the density and other ground-state properties. Assume that N interacting electrons are moving in an external potential $v(\underset{\sim}{r})$, for instance the potential of the nuclei of the system. The Hamiltonian is

$$H = T + U + V \quad ,$$

where T is the kinetic energy operator, U is the electron-electron interaction term and V is the external potential operator corresponding to the potential $v(\underset{\sim}{r})$. In principle, the corresponding density $n(\underset{\sim}{r})$ can be calculated. Thus for a given potential $v(\underset{\sim}{r})$ the density is uniquely determined. The converse statement is less trivial, but has been proven in the following way |3|: Assume that the same density is obtained for a different potential $v'(\underset{\sim}{r})$ which differs from $v(\underset{\sim}{r})$ by more than a trivial constant. The ground-state ψ' for the potential $v'(\underset{\sim}{r})$ is different from the ground-state ψ for the potential $v(\underset{\sim}{r})$, since they satisfy different Schrödinger equations. If the ground-state is nondegenerate |6|, the expectation value of the Hamiltonian has its lowest value for the exact ground-state wave function and

$$\begin{aligned} E' &= \langle\psi'|H'|\psi'\rangle \; < \; \langle\psi|H'|\psi\rangle \\ &= \langle\psi|H+V'-V|\psi\rangle = E + \int \left[v'(\underset{\sim}{r})-v(\underset{\sim}{r})\right] n(\underset{\sim}{r})\, d^3r \end{aligned} \tag{1}$$

However, the primed and unprimed quantities can be interchanged giving

$$E < E' + \int \left[v(\underset{\sim}{r}) - v'(\underset{\sim}{r})\right] n(\underset{\sim}{r})\, d^3r \tag{2}$$

Adding (1) and (2) we obtain

$$E + E' < E + E'$$

which disproves our assumption that there are two potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ (differing by more than a constant) which give the same density $n(\mathbf{r})$. Thus there exists only one $v(\mathbf{r})$ which gives rise to the density $n(\mathbf{r})$, and $v(\mathbf{r})$ can be considered a functional of $n(\mathbf{r})$ |8|. Once $v(\mathbf{r})$ is known ψ can, in principle, be calculated and all ground-state properties can be determined. It follows that all ground-state properties are functionals of the density, which is one of the basic results.

Examples of such functionals are the kinetic and electron-electron interaction energies and we call **their sum F[n]**

$$F[n] = <\psi \ |T + U| \ \psi> \tag{3}$$

For a given potential $v(\mathbf{r})$ we define

$$E_v[n] = \int v(\mathbf{r}) \ n(\mathbf{r}) \ d^3r + F[n] \tag{4}$$

For the correct ground-state density $n(\mathbf{r})$ the functional $E_v[n]$ is equal to the ground-state energy E. This is actually the lowest value $E_v[n']$ can obtain for any density $n'(\mathbf{r})$ having the correct number of electrons

$$\int n'(\mathbf{r}) \ d^3r = N \tag{5}$$

This variational principle is proven as follows |3|: Consider a state ψ' which is not the ground-state of H. Then

$$\begin{aligned} E_v[n] &= <\psi|H|\psi> \ < \ <\psi'|H|\psi'> \\ &= <\psi'|V+T+U|\psi'> = \int v(\mathbf{r}) \ n'(\mathbf{r}) \ d^3r + F[n'] = E_v[n'] \end{aligned} \tag{6}$$

where we have used the definition (3).

To summarize, we have shown that there exists a universal (of $v(\mathbf{r})$ independent) functional $F[n]$ which gives the total energy via Eq. (4) and that the functional $F_v[n]$ in Eq. (4) has its minimum for the correct ground-state density. This gives us a general method for calculating ground-state properties: (a) Find an approximate functional $F[n]$ and (b) minimize $E_v[n]$.

An example of this approach is the Thomas-Fermi method |9|, in which it is assumed that the electrons are independent and that the kinetic energy density is the same as for a homogeneous medium. Then we obtain

$$F[n] = \frac{e^2}{2} \int \frac{n(\mathbf{r}) \ n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ d^3r \ d^3r' + C \int [n(\mathbf{r})]^{5/3} \ d^3r \quad ,$$

where C is a numerical constant. To minimize $E_v[n]$, we use the corresponding Euler equation which in this case is the well-known Thomas-Fermi equation [9].

2.2. Derivation of a Hartree-like Equation

Although the Thomas-Fermi method gives a qualitative picture of, for instance, an atom, it is too crude for detailed quantitative calculations. Actually, to find good approximations for the functional F[n] is very difficult and the method introduced by Kohn and Sham [4] is therefore of great importance. They realized that it is possible to separate (numerically) large contributions to F|n| which can be treated exactly, so that only the smaller reminder has to be treated approximately. Thus they used the partitioning

$$E_v[n] = \int v(\mathbf{r})\, n(\mathbf{r})\, d^3r + \frac{e^2}{2} \int \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d^3r\, d^3r' + T_s[n] + E_{xc}[n] \tag{7}$$

The second term is the electrostatic interaction energy and the third is the kinetic energy of <u>noninteracting</u> electrons with the density $n(\mathbf{r})$. The final term is the exchange correlation energy, which would be zero if the electrons were noninteracting. For interacting electrons it contains all the many-body effects. The density is now varied under the constraint

$$\int \delta n(\mathbf{r})\, d^3r = 0$$

to find the minimum of $E_v[n]$. We obtain the Euler equation

$$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{eff}(\mathbf{r}) \right\} d^3r = 0 \tag{8}$$

with

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|r-r'|}\, d^3r' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \tag{9}$$

Kohn and Sham observed that Eq. (8) is identical to the equation for noninteracting electrons moving in the potential $v_{eff}(\mathbf{r})$. Therefore we can solve Eq. (8) by using the Hartree method

$$\left\{-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r})\right\} \psi_\nu(\mathbf{r}) = \varepsilon_\nu\, \psi_\nu(\mathbf{r}) \tag{10}$$

$$n(\mathbf{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\mathbf{r})|^2 \tag{11}$$

For a given functional $E_{xc}[n]$ Eqs. (9)-(11) are solved by a self-consistent approach; we guess a density which, via Eq. (9), gives an effective potential and, via Eqs. (10)-(11), a new density.

It should be emphasized that this is a method for calculating ground-state properties. The energy eigenvalues ε_ν and eigenfunctions $\psi_\nu(\mathbf{r})$ of Eq. (10) have not been shown to be excitation energies and wave functions, respectively, but are only auxiliary quantities obtained in the calculation of the density. The quantities that can be calculated are the electron density, the total energy and properties which can be derived from these quantities. For a chemisorbed atom or molecule, for example, we can obtain the binding energy, the equilibrium geometry (i.e. adsorption site and separation distance), the vibration frequencies (if the Born-Oppenheimer approximation is used), the activation energy for diffusion and the dipole moment.

The equation (10) is a one-body equation, i.e. the normal electron-electron interaction term

$$\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}$$

does not enter explicitly. This is the main reason to the simplicity of this approach. Furthermore, the potential is local, in contrast to, for example, the Hartree-Fock potential

$$V_{HF}\, \psi(\mathbf{r}) = \int V_{HF}(\mathbf{r},\mathbf{r}')\, \psi(\mathbf{r}')\, d^3r' \qquad (12)$$

Actually, if the so-called local density approximation (see below) is used for $E_{xc}[n]$ Eqs. (9)-(11) are not more difficult to solve than the Hartree equations.

The importance of the method of Kohn and Sham can be illustrated by some typical numbers. Fig. 1 shows the partitioning of the valence contribution to the total energy for a manganese atom. The kinetic energy, T_s, the electrostatic interaction between the valence electrons and the core, E_{vc}, and the electrostatic interaction between the valence electrons, E_{vv}, are all treated exactly. Only the exchange energy, E_x, and the correlation energy, E_c, (not shown in the figure, but substantially smaller than E_x) require approximation. Note the contrast to attempts of approximating the functional $F[n]$ directly, e.g., the Thomas-Fermi method, in which case also the large term T_s is treated approximately.

The numbers in Fig. 1 do not mean, of course, that exchange and correlation effects can be neglected. On the contrary, for the calculation of many properties good approximations for E_x and E_c are needed.

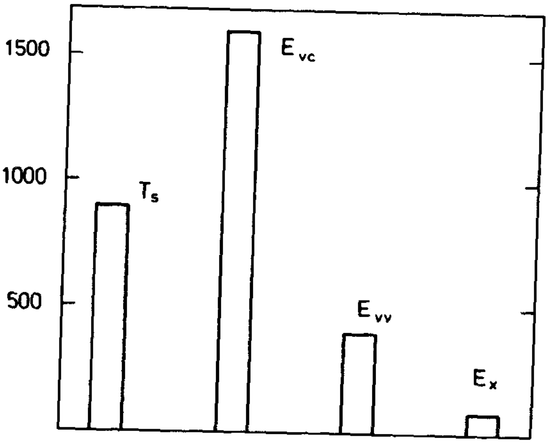

Fig. 1: The kinetic energy of the valence electrons (T_s), the core-valence (E_{vc}) and valence-valence (E_{vv}) electrostatic interaction energies and the valence exchange energy (E_x) for a manganese atom |18|. All energies are given in eV.

2.3. The Local Density Approximation

The most commonly used approximation is the local density (LD) approximation, which assumes that the electron density variations are spatially slow. Consider an electron at a point r in space. If the density varies little over some typical distance, say a few inverse Fermi wave vectors, this electron "sees" an essentially homogeneous medium. Then we can associate an exchange-correlation energy to this electron which is the same as for an electron in a homogeneous medium with the density $n(\underset{\sim}{r})$. For the total exchange-correlation energy we obtain |3,4|

$$E_{xc}[n] \approx \int n(\underset{\sim}{r})\, \varepsilon_{xc}(n(\underset{\sim}{r}))\, d^3r \qquad (13)$$

where $\varepsilon_{xc}(n(\underset{\sim}{r}))$ is the exchange-correlation energy per particle for a homogeneous system with the density $n(\underset{\sim}{r})$. Inserting this approximation in Eq. (9) gives us the exchange-correlation contribution to the effective potential

$$v_{xc}(\underset{\sim}{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n(\underset{\sim}{r})} \quad \frac{\partial}{\partial n(\underset{\sim}{r})} \{n(\underset{\sim}{r})\, \varepsilon_{xc}(n(\underset{\sim}{r}))\} \qquad (14)$$

This potential is not only local in the sense mentioned above (Eq. (12)) but it has also a local density dependence, i.e. $v_{xc}(\underset{\sim}{r})$ depends on the density at the point $\underset{\sim}{r}$ only.

The LD approximation can be extended to spin-polarized systems. The basic quantities are now the density of spin-up and spin-down electrons, $n_+(\underset{\sim}{r})$ and $n_-(\underset{\sim}{r})$, respectively. We obtain |10,11,7| the local spin density (LSD) approximation

$$E_{xc}[n_+,n_-] \approx \int n(\underset{\sim}{r})\ \varepsilon_x(n_+(\underset{\sim}{r}),\ n_-(\underset{\sim}{r}))\ d^3r \qquad (15)$$

with obvious notation. It should be noted that Eq. (15) is not rotationally invariant in spin space.

If correlation effects are neglected in Eq. (13), we get

$$E_{xc}[n] \approx \int n(\underset{\sim}{r})\ \varepsilon_x(n(\underset{\sim}{r}))\ d^3r = \frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} \int [n(\underset{\sim}{r})]^{4/3}\ d^3r \qquad (16)$$

where ε_x is the exchange energy per particle of a homogeneous system. The corresponding potential (Eq. (14)) is

$$v_{xc}(n(\underset{\sim}{r})) = \mu_x(r_s) = -1.22/r_s \ \ \mathrm{Ry}$$

where r_s is given by

$$\frac{4\pi}{3}(r_s a_o)^3 = \frac{1}{n(\underset{\sim}{r})}$$

Results for ε_{xc} and v_{xc} including correlation effects have been given in the literature |12,10,7|. For instance, in the absence of spin polarization we have |12|

$$v_{xc}(n(\underset{\sim}{r})) = \beta(r_s)\ \mu_x(r_s)$$

$$\beta(r_s) = 1 + 0.0368\ r_s\ \ln\left(1 + \frac{21}{r_s}\right)$$

The function $\beta(r_s)$ describes correlation effects. It has a fairly weak dependence on r_s, as is shown in Fig. 2.

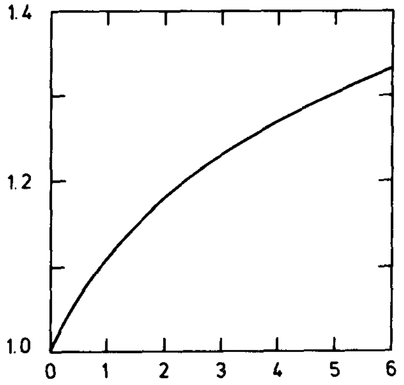

Fig. 2 : The function $\beta(r_s)$ which describes the effects of correlation on the exchange-correlation potential v_{xc}. If correlation is neglected $\beta(r_s) \equiv 1$ and in the $X\alpha$ approximation $\beta(r_s)$ is replaced by a constant $3\alpha/2$ (after Ref. |12|).

A slightly different approximation, the so-called Xα approximation, was proposed by Slater |5| who, in essence, multiplied Eq. (16) by a constant 3 / 2 and obtained

$$E_{xc}[n] \approx \frac{3}{2}\alpha \int n(\underset{\sim}{r})\, \varepsilon_x(n(\underset{\sim}{r}))\, d^3r$$

This approach gives the so-called Xα potential

$$v_{X\alpha}(n(\underset{\sim}{r})) = \frac{3}{2}\alpha\, \mu_x(r_s)$$

The case α=2/3 is sometimes referred to as the Dirac-Gâspâr-Kohn-Sham |13,4| potential, and α=1 gives the Slater potential. Schwarz has proposed the use of an atom-dependent value of α which for most atoms is in the range 0.70-0.75 |14|. If these values of α are used, the Xα and LD approximations give fairly similar results for systems without spin-polarization. However, the spin-dependent version of the Xα approximation gives a stronger spin-dependence than the LSD approximation |15,16| and it overestimates, for instance, the tendency to ferromagnetism for transition metals.

As discussed below, it is not at all clear a priori that approximations (13)-(15) are valid for the systems of interest. It is therefore of great importance that these approximations have now been tested for a large number of systems such as atoms |17,7,18|, small molecules |15,19,20|, simple and transition metals |21-23| and compounds |24|. As examples we show in Fig. 3 the ionization potential of a large number of atoms and in Fig. 4 the binding energy, the equilibrium separation and the vibration frequency of diatomic molecules. The molecular results are discussed in detail by R.O. Jones in this volume.

Generally good agreement with experiment is obtained. For instance, the ionization energy of atoms is typically 1/2 eV in error, the binding energy of small molecules is correct within 2 eV and the cohesive energy of metals within 1/2-1 eV. The errors for the separation distance is typically of the order 1/10 atomic unit. Usually the results are somewhat worse for the 3d series than for other series. This has been discussed extensively by Harris and Jones for atoms and diatomic molecules |25|. However, the magnetic properties of the 3d metals at zero temperatures seem to be described well |16,21-23|.

2.4. Nonlocal Functionals

In the LD approximation $\varepsilon_{xc}(\underset{\sim}{r})$ and $v_{xc}(\underset{\sim}{r})$ depend only on the "local" density $n(\underset{\sim}{r})$. In general there should be a dependence on the density at all points in the neighbourhood of $\underset{\sim}{r}$. Two such approximations were proposed in the original papers |3,4|. The LD approximation can be viewed as the lowest order term in a gradient expansion. Including the next term we obtain |3,4|

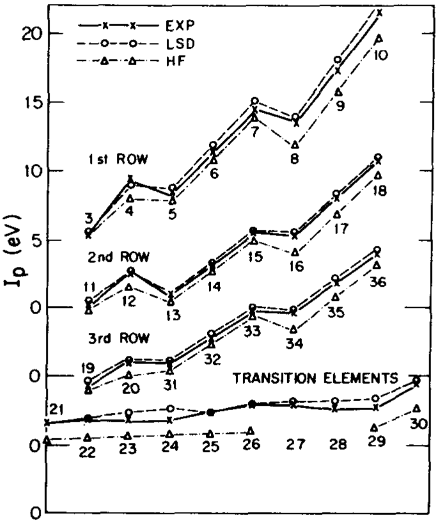

Fig. 3 : The first ionization potential of atoms in the LSD and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. The zero of energy is shifted 5 eV, 10 eV and 15 eV for the second row, the third row and the transition element series, respectively (after Ref. |18|).

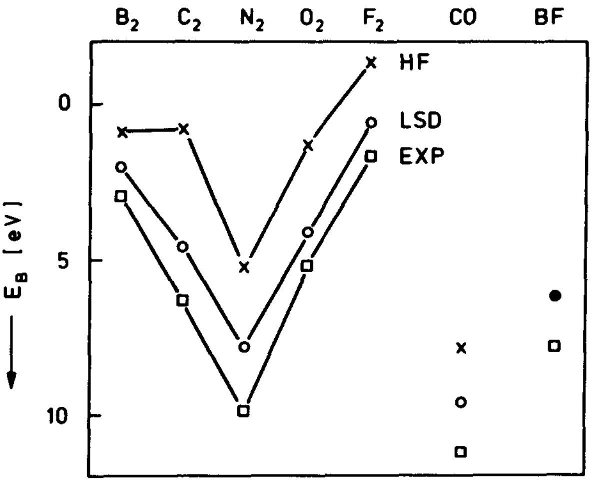

Fig. 4 : The binding energy of first-row molecules in the LSD and HF approximations compared with experiment. The LSD results are calculated in the LMTO method |19| using a limited basis set and larger binding energies would be obtained if the basis set were complete (after Ref. |19|).

$$E_{xc}[n] \approx \int n(\underset{\sim}{r})\, \varepsilon_{xc}(n(\underset{\sim}{r}))\, d^3r + \int C(n(\underset{\sim}{r}))\, \frac{|\nabla n(\underset{\sim}{r})|^2}{[n(\underset{\sim}{r})]^{4/3}}\, d^3r \ , \tag{18}$$

where $C(n(\underset{\sim}{r}))$ is a function |26| of the density. It is also possible to sum all terms which are of second order in the density variations, giving |3,4,27|

$$E_{xc}[n] \approx \int n(\underset{\sim}{r})\varepsilon_{xc}(n(\underset{\sim}{r}))d^3r - \frac{1}{4} \iint K_{xc}(\underset{\sim}{r}-\underset{\sim}{r}',n)(n(\underset{\sim}{r})-n(\underset{\sim}{r}'))^2 d^3r d^3r' \tag{19}$$

where $K_{xc}(\underset{\sim}{r}-\underset{\sim}{r}',n)$ is related to the dielectric function of a homogeneous medium with the density n. The density argument n is in general not uniquely specified by the theory.

The functional (19) is exact in the limit of weak density variations

$$n(\underset{\sim}{r}) = n_o + \Delta n(\underset{\sim}{r}) \tag{20}$$

with

$$|\Delta n(\underset{\sim}{r})| << n_o$$

In this limit it is therefore possible to compare the gradient expansion (18) and the LD approximation (13). It is questionable whether the gradient expansion improves the LD approximation in this limit for density variations having wave lengths typical for most systems |28,29|. In the more realistic situation of strong density variations the gradient expansion has primarily been applied to atoms |30| and surfaces |31-34|.

In the calculations for atoms, Herman et al |30| obtained improvements by treating $C(n(\underset{\sim}{r}))$ as an adjustable parameter. However, if the first principles results |26| for $C(n(\underset{\sim}{r}))$ are applied to atoms the correction to the LD result for the total energy has the wrong sign. In the surface applications the work function and surface energy were calculated. For the work function numerically very different results have been obtained. Rose et al |33| found an almost negligible correction due to the gradient term while Lau and Kohn |31| obtained a substantial contribution which made the agreement with experiment worse. For the surface energy Lau and Kohn |31| found worse agreement when gradient terms are included, while Rose et al |33| claimed improved agreement. As the experimental results for the surface energy are fairly uncertain Perdew et al |35| instead considered a simple model for the surface, where the contributions from different wave vectors were considered. The results for the surface energy were compared with the ones of the gradient expansion and Perdew et al concluded that the gradient expansion gives too large corrections and is inappropriate for surfaces.