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NEW ASPECT OF CALCULATIONS OF THE ELECTRONIC STRUCTURE OF MAGNETIC MATERIALS[1]

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Recent developments in the calculation of the electronic structure of solids, with special respect to magnetic materials, are reviewed. The spin density functional method is explained and the results based on this method are compared with the Hartree-Fock calculations. Various computational schemes are mentioned and on representative examples the usefulness of these methods for our understanding of magnetic properties is demonstrated.

НЕКОТОРЫЕ НОВЫЕ АСПЕКТЫ ВЫЧИСЛЕНИЯ ЭЛЕКТРОННОЙ СТРУКТУРЫ МАГНИТНЫХ МАТЕРИАЛОВ

В работе приводится обзор современного состояния вычислений электронной структуры твердых тел, причем особое внимание уделяется магнитным материалам. Объясняется метод функционала спиновой плотности, а результаты, полученные на основе этого метода, сравниваются с вычислениями по методу Хартрифока. Приведены также разные схемы вычислений и на характерных примерах продемонстрирована полезность этих методов для нашего понимания магнитных свойств материалов.

I. INTRODUCTION

During the past few years a qualitative change in the calculation of the electronic structure of solids has occurred. Both the advanced computing technique and the new physical concept discussed below allow now a relatively reliable determination of the electronic structure of real substances from the first principles (i.e., only the geometry of the system and the atomic numbers of the participating atoms are given as input data). Such calculations yield beside the distribution of electrons various other physical quantities as the binding energies, equilibrium geometry, elastic properties, etc.

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Beginning approximately five years ago, similar procedures were also applied to calculate the magnetic properties of solids. To realize how subtle this problem is, let us consider the case of nickel. The total energy of an Ni atom is ~1500 a.u.; the exchange energy which controls the magnetism of metallic nickel is only a tiny franction of it (~0.01 a.u.). Yet to calculate the exchange we have to substract the total energies of systems differing in spin [1], i.e., quantities which are many orders of magnitude larger. The virtue of the local spin density functional method on which the bulk of the results is based does not lie, however, in the precise evaluation of the total energy, it rather gives a good description of the changes which occur in the valence states of the electrons when the solid is formed.

II. LOCAL SPIN DENSITY FUNCTIONAL METHOD

The principal problem of any electron structure calculation is to find an (approximative) solution of the Schrödinger equation for the system of interacting electrons placed in an external field. The corresponding hamiltonian consists of the kinetic energy of electrons, the interaction V_{ext} of electrons with the external field and the interelectron Coulomb repulsion V_{ee}. It is the last term which makes the problem difficult to solve: for the following discussion we rewrite it as a sum of interaction of a given electron with the charge density ϱ produced by the whole electron system and the s.c. exchange-correlation term V_{xc}, the form of which will be specified later

$$V_{ee} = \sum_{k=1}^{N} \left[\int \frac{\varrho(r')}{|r_k - r'|} \, dr' + V_{xc}^{(k)} \right]. \tag{1}$$

In the Hartree method $V_{xc}^{(k)}$ is simply the selfinteraction of the k-th electron taken with the minus sign (the electron does not interact with itself). The many-electron problem is then reduced to the single-electron one. The Schrödinger equation for the one-electron functions being

$$\left[-\frac{1}{2}\nabla^2 + V_{ext} + \int \frac{\varrho(r')}{|r-r'|} \, dr' + V_{xc}^{(k)} \right] \varphi_k(r) = E_k \varphi_k(r) \tag{2}$$

with $V_{xc}^{(k)}(\text{Hartree}) = -\int \frac{\varphi_k^*(r')\varphi_k(r')}{|r-r'|} \, dr'$; $\varrho = \sum_{k=1}^{N} \varphi_k^* \varphi_k$. The Hartree-Fock (HF) formulation differs from the Hartree method by respecting the Pauli exclusion principle. It leads to the same equation, only the exchange-correlation potential is more complicated

$$V_{xc}^{(k)}(\text{HF}) = \frac{-\sum_{j=1}^{N} \int \frac{\varphi_k^*(r)\varphi_j^*(r')\varphi_j(r)\varphi_k(r')}{|r-r'|} \, dr'}{\varphi_k^*(r)\varphi_k(r)}. \tag{3}$$

Though the reduction of the many-electron problem to the single-electron one makes the solution feasible for small systems, the calculation of the electron structure of solids is still formidable. The approximation to the HF procedure called commonly the Xα method was, therefore, developed (see [1] for details). In this method $V_{xc}^{(\text{HF})}$ is approximated by

$$V_{xc}(X\alpha) = -3\alpha \left(\frac{3}{8\pi} \varrho \right)^{1/3}, \tag{4}$$

where the parameter α, $2/3 \leq \alpha \leq 1$ is fixed for each atom by a supplementary condition (usually that HF atomic energy is equal to the Xα one).

It must be emphasized that in the HF method the electrons are not correlated and costly perturbation procedure (configuration interaction) are employed to take the correlation into account.

In mid-sixties Hohenberg, Kohn and Sham [2—3] suggested an entirely new approach to the calculation of the electron structure. They noted that for the ground state of the many-electron system (with a fixed number of electrons) all the physical quantities, in particular the total energy, may be expressed as functionals of the electron density. Moreover, the true density is such that it minimizes the total energy of the system. Variation of the density so that the energy (consisting of kinetic, potential and exchange-correlation parts) becomes minimal, leads to the equation

$$\left[-\frac{1}{2}\nabla^2 + V_{ext} + \int \frac{\varrho(r')}{|r-r'|} \, dr' + \tilde{V}_{xc} \right] \psi_k = \varepsilon_k \psi_k, \tag{5}$$

where $\tilde{V}_{xc} = \delta E_{xc}/\delta\varrho$ is the functional derivative of the exchange-correlation part of energy with respect to the density. In (5) ϱ is connected with ψ_k by

$$\varrho = \sum_{k=1}^{N} \psi_k^* \psi_k. \tag{6}$$

The equation (5) is formally the same as (2) but we note that no approximation has been made up to this point. To make the Hohenberg–Kohn–Sham scheme useful, the form of V_{xc} (and consequently E_{xc})must be specified. The usual way is to relate E_{xc} to the exchange-correlation energy of the homogeneous (but interacting) electron gas neutralized by a homogeneous positive background, which system may be solved with sufficient accuracy. Interpolation formulae are available for so determined V_{xc}; e.g., according to Hedin and Lundquist [4]

$$\tilde{V}_{xc} = -3\beta(r_s) \left[\frac{3}{8\pi} \varrho \right]^{1/3}; \tag{7}$$

$$\beta(r_s)=\frac{2}{3}[1+0.0316r_s \ln(1+24.3/r_s)]$$

with $r_s=\left[\frac{4}{3}\pi\varrho\right]^{-1/3}$.

The aproximation called the local spin density functional (LSD) method assumes that V_{xc} determined in this way is valid also in inhomogeneous systems. Comparing (5—7) with (2) and (4) we see that LSD equations are identical with the Xα ones only in the LSD method, the parameter α is substituted by the quantity β depending on the density which, however, causes almost no difference in computational procedures. We see, therefore, that the LSD method is much simpler compared to HF and yet it takes into account the correlation between electrons. The price we have to pay for it may be summarized as follows:

(i) No simple connection between ε_i, ψ_i in (5) and the one-electron energies and wave functions exists. The question as to which extent ε_i and ψ_i may be used to represent the single electron quantities is still under discussion.

(ii) As a consequence of the previous point the total energy is not simply the sum of ε_i but it is given by the expression

$$E=\sum_{i=1}^{N}\left[\varepsilon_i-\frac{1}{2}\langle i|V_c|i\rangle-\frac{1}{4}\langle i|\bar{V}_{xc}|i\rangle\right]; \qquad V_c=\int\frac{\varrho(r')}{|r-r'|}\,dr'.$$

(iii) The LSD method applies only to the ground state (but excited states with a symmetry different from the ground state may be treated similarly).

Without difficulty the LSD method may be generalized for magnetic problems by introducing V_{xc} potentials depending on the spin of electrons (see e.g. [5]).

From the above discussion it follows that the LSD method treats the correlation properly, while neglecting the inhomogeneity of the electron system. For HF calculations the situation is just reverse and it is thus desirable to compare results obtained by these methods. Particularly suitable subjects for such comparison are atoms for which sufficiently reliable experimental results are available and the calculations are not obscured by additional approximations we have to make in more extended systems. In Fig. 1 the accuracy with which HF, Xα, and LSD methods fit the experimentally observed ionization energies of light atoms is shown. The corresponding relative root-mean-square deviations are 2.4 % (LSD), 5.4 % (HF) and 6.5 % (Xα), thus documenting the convencience of the LSD method.

A very interesting comparison of the three methods, when calculating the atomic multiplet structure, has recently been made by Wood [7]. Also in this case the LSD gives the best results (see Fig. 2 for an example), though, in order to calculate the multiplet structure, the functions ψ_k appearing in (5) are treated as genuine electron orbitals.

A demanding test of atomic calculations is the determination of the Fermi

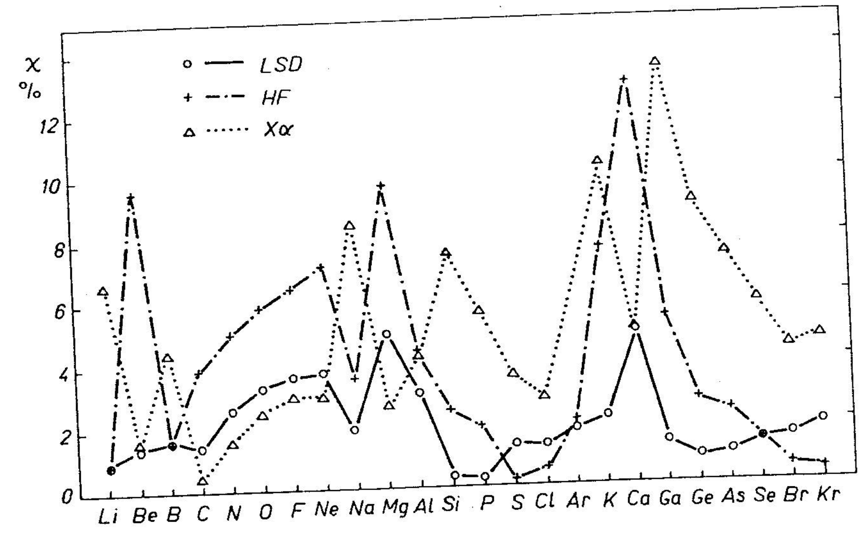

Fig. 1. Quantity $\chi=|E^{exp.}_{ionis.}-E^{calc.}_{ionis.}|/E^{exp.}_{ionis.}$ for light atoms (after [6]). Experimental ionization potentials were corrected for the multiplet splitting.

contact term χ, which is proportional to the difference between spin up and spin down electron densities at the nucleus. For the alkali metal atoms, where the dominant contribution to χ gives the unpaired s-electron, all the three methods give a fair agreement with experiment. On the other hand, none of these methods is capable to explain χ in atoms, where it arises due to the polarization of s-electrons by the unpaired electrons in p or d shells [8].

III. COMPUTATIONAL PROCEDURES

A common feature of the computational methods based on LSD is that they are selfconsistent, i.e., starting with the guessed functions ψ_k the density (6) is calculated and with the potential (7) the equation (5) is solved. As a result new functions ψ_k are obtained and the whole procedure is repeated until two subsequent iterations give identical results. Most of the methods may be equally well applied to ionic, covalent and metallic substances and, moreover, modifications for finite systems (clusters, molecules) as well as for infinite crystals exist.

The methods may be divided into those using and those which do not employ the muffin-tin potentials. The muffin-tin approximation (i.e. around each atom the potential is assumed to have a spherical symmetry inside the muffin-tin sphere and it is approximated by a constant inbetween the spheres) greatly facilitates the computation. To the most efficient procedure there belong the augmented-spherical-wave (ASW) [9] and the linear augmented plane wave (LAPW) [10] methods. For clusters the multiple scattering cluster (MSC) method (see [1] for detailed discussion) and a version of the LMTO program (linear combination of the muffin-tin orbitals) [11] are available. The drawback of the muffin-tin methods is that a somewhat deliberate choice of the radii of muffin-tin spheres must be made, also the asssumption of the spherical symmetry of the potential may not be justified in systems with a symmetry far from the spherical one (planar complexes, surfaces, etc.).

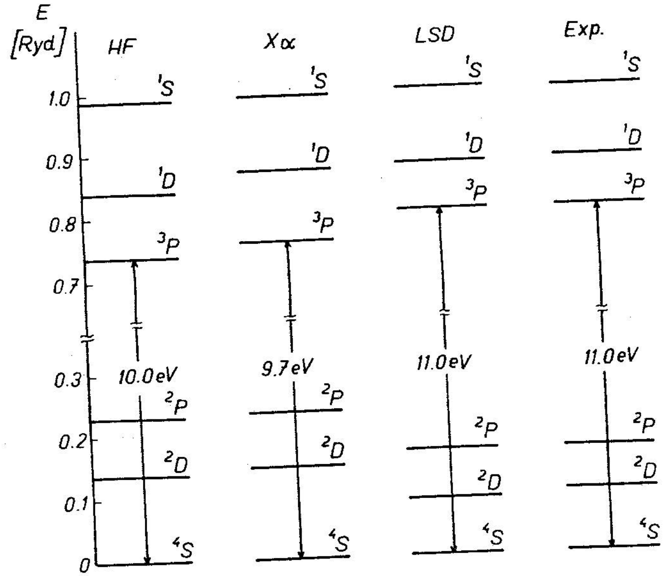

Fig. 2. Multiplet structures of P and P^+ [7].

The procedures not using the muffin-tin are direct descendants of the linear combination of the atomic orbital method. In the discrete variational (DV) method [12] a grid of sampling points is chosen in which the Schrödinger equation is integrated numerically. In the Gaussian type orbitals method [13] the Gaussian functions centred on individual atoms are employed as the LCAO basis set. When the exchange-correlation potential and the density are also expanded in terms of Gaussian functions, all the matrix elements may be calculated analytically. Both the DV and the GTO methods may be used to calculate the electronic structure of molecules, clusters as well as the band structures of crystals.

IV. RESULTS

Insulators

A number of calculations of the electron structure of transition metal complexes now exists. The clusters containing $3d$ ions (e. g. [14]) as well as those with the RE [15] and actinides [16] were studied mostly using the MSC or the DV methods. The calculations yield the distribution of the magnetic moment (e.g. in [17] the spin density in YIG which accounted well for the experimental results was determined) and a good insight into the nature of the chemical bonding is gained. However, so far nobody has attempted the calculation of the multiplet structure and also the direct comparison of the LSD energies ε_k (eq. (5)) with experimental XPS spectra is somewhat dubious due to the unclear connection between ε_k and the single electron energies (§ 2). Often the Xα potential has been used (the difference between Xα and LSD potentials being smaller compared to other approximations made).

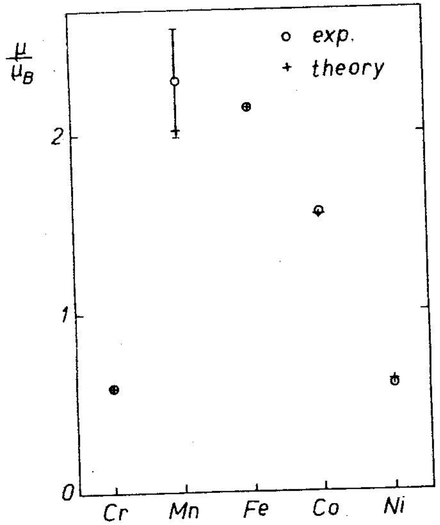

Fig. 3. Magnetic moments of the $3d$ transition metals [18—19]. μ of γ-Mn was calculated at the experimental lattice constant, for chromium the spin density wave was not taken into account.

Metals

LSD methods were successfully applied to study the magnetism of pure metals. Moruzzi et al. [18] calculated by a modified KKR method the properties of ferromagnetic Fe, Ni, and Co, recently Kübler [19] has used the ASW method to study antiferromagnetic chromium and γ-manganese. Calculated magnetic moments μ (Fig. 3) agree very well with experiment and also the pressure derivatives are at least qualitatively explained. The electronic structure of ferromagnetic Ni was also determined using the GTO method [20]. It was shown that the LSD potential gives better results here compared with the Xα result.

Surface and impurities

A study of surface states, surface magnetization and the electron polarization of Ni (001) using the DV method has recently been reported by Wang and Freeman [21]. In particular no dead layer was found (the surface layer had 40 % of the bulk magnetic moment), nine layers were adequate to get the bulk behaviour inside the metal and the calculation indicated a Friedel-type oscillation of the magnetic moment as a function of the distance from the surface.

The formation of the magnetic moment on the impurities in metals is one of the most interesting problems to solve in the theory of magnetism. Using the LSD formalism Ellis et al. [22] developed a model for Fe, Co and Ni impurities in β'-NiAl and Zeller et al. [23] studied impurities in the noble metals Cu and Ag.

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