# Iterative LCAO treatment with overlap and band occupation in the iron-group metals

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# Iterative LCAO treatment with overlap and band occupation in the iron-group metals (*)

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**Résumé.** — Le modèle de combinaisons linéaires d'orbitales atomiques a été appliqué à l'étude des bandes s et d des métaux du groupe du fer en portant une attention particulière à : (a) le choix de la base d'orbitales atomiques et des ajustements nécessaires pour reproduire les résultats du modèle de l'atome renormalisé ; (b) l'influence du recouvrement et du nombre d'interactions entre voisins sur les résultats (les calculs de la bande s nécessitent en principe de tenir compte des douze premières couches atomiques, tandis que pour la bande d, la première et parfois la seconde couche suffisent) ; (c) l'égalisation des niveaux de Fermi pour déterminer les occupations et les positions relatives des bandes s et d en négligeant l'hybridisation s-d. Les résultats obtenus à partir de paramètres de liaisons fortes (niveaux atomiques, intégrales de saut) estimés par des calculs de chimie quantique sont en bon accord général avec les calculs de structure de bandes. On trouve pour les nombres d'occupations de la bande s pour le Ni, Co et Fe, CFC, respectivement les valeurs de 0,85, 0,92 et 0,88 et pour la distance entre le bas de la bande s et le centre de la bande d, les valeurs respectives de 10,33 eV, 10,04 eV et 7,08 eV.

**Abstract.** — A study of the LCAO scheme for the iron-group s- and d-bands is carried out with special emphasis on : (a) the choice of the AO basis and its adjustment to reproduce approaches like the renormalized-atom ansatz ; (b) the dependence of the final results on overlap and the number of neighbours taken into account (s-band calculations require at least neighbours from up to the 12th shell, whereas for d-band 2nd neighbours are required at worst) ; (c) principle of Fermi-level equalization as a technique for determining the occupations and the relative positions of the s- and d-bands in an approximation neglecting s-d coupling. The results, obtained using quantum-chemical expressions for the « atomic » levels and for the hopping integrals, are *consistent* with the previous calculations, although they differ in many details. The estimated s-band occupation numbers for fcc Ni, Co and Fe are 0.85, 0.92 and 0.88, respectively, and the s-d separations (bottom of the s-band to the centre of the d-band) are 10.33 eV, 10.04 eV and 7.08 eV, respectively.

Great progress has been made in recent years in the quantum theory of transition metals. However, many points still need clarification even at the level of simple band-theory. This note is devoted to three of those points : (a) the nature of the Atomic Orbitals (AO) to be used in LCAO calculations ; (b) the possibility of a satisfactory LCAO (TB) calculation with overlap even for the s-band ; (c) the distribution of electrons among the s- and d-bands when they are treated separately.

**1.** — The nature of the *in situ* AO's has been the subject of much research especially as regards d-orbitals [1, 2]. In addition to TB treatments where parameters were directly adjusted, there have been the renormalized-atom approach (RAA) [3] and the resonance approach [4]. These approaches correspond to opposite points of view : in the former, the d

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orbitals of different atoms are directly coupled to one another, but are contracted so as to affect the s band in a way which depends on the packing; in the latter, each d orbital is spread into a continuum, each component of the d-band involving a different d orbital.

The above effects (both of which are probably physically significant and would somehow coexist in a treatment taking all details into account) can be formulated in the frame of the LCAO scheme, if each atom is assigned a multiple-$\zeta$ basis capable of producing sufficiently flexible d-orbitals. We illustrate this point on the example of the RAA.

As is well known, the radial factors $R_{nd}$ of the Hartree-Fock d orbitals of any free atom can be approximated by linear combinations of several Slater-type orbitals (STO). The five-STO form is a very good approximation [5]. For the ground states $^2$D 3d$^9$4s$^0$ of Ni$^+$ and $^3$D 3d$^9$4s of Ni, it can be written :

$$R_{3d} = \frac{4\,r^2}{3\sqrt{10}} \sum_j^5 c_j\, \zeta_j^{7/2} \exp(-\zeta_j\, r) \qquad (1)$$

the values of the parameters $c$ and $\zeta$ being those given in table I.

Table I

| | Ni$^+$ | | Ni | | Renorm. Ni |
|---|---|---|---|---|---|
| $j$ | $\zeta$ | $c$ | $\zeta$ | $c$ | $c'$ |
| 1 | 12.83200 | 0.02520 | 11.84520 | 0.03219 | 0.04887 |
| 2 | 7.12077 | 0.20378 | 6.96821 | 0.21853 | 0.32874 |
| 3 | 4.75253 | 0.33129 | 4.58757 | 0.30420 | 0.41692 |
| 4 | 2.78709 | 0.41773 | 2.95021 | 0.37397 | 0.31379 |
| 5 | 1.57027 | 0.21053 | 1.58997 | 0.26745 | 0 |

The d orbitals of Ni atoms in the crystal may be expected to be linear combinations of type (1) lying somewhere between those of Ni and those of Ni$^+$. Now, the orbital exponents $\zeta$ of the two species are very close to one another : therefore, in order to take the packing into account, we can accept the orbital exponents of the neutral atom and just modify the coefficients $c$ so as to satisfy conditions similar to those of the RAA. To provide some criterion based on a reasonably continuous damping of the tails of the various STO components, we can weigh the coefficients of the fourth column of table I by factors

$$d_j = (1 - \exp(1.58997 - \zeta_j))^2 \qquad (2)$$

and renormalize. This procedure is no more arbitrary than the RAA prescription. The coefficients obtained are shown in the fifth column of table I. The relative importance of the two radial functions before and after weighing according to equation (2) is illustrated by the following values :

| | Free atom | | *in situ* (Eq. (2)) | |
|---|---|---|---|---|
| $R$(Ni-Ni) | $R_{3d}$ | $S_\sigma^{dd}$ | $R_{3d}$ | $S_\sigma^{dd}$ |
| 1.246 (*) | $2.07 \times 10^{-2}$ | ... | $6.36 \times 10^{-3}$ | ... |
| 1.495 | $8.13 \times 10^{-3}$ | ... | $1.48 \times 10^{-3}$ | ... |
| 2.492 (**) | $3.26 \times 10^{-4}$ | 0.0324 | $5.41 \times 10^{-6}$ | 0.0025 |

(*) centre of the standard Ni-Ni bond
(**) standard bond distance

The above technique can be used to obtain energy-dependent AO's and, of course, the LCAO form of density-functional approaches. Before entering those studies, however, a more accurate analysis is needed, since even the results for reasonably reliable free-atom orbitals are not known. This is especially interesting in cases such as nickel, where the d$^9$s and the d$^8$s$^2$ configurations are practically degenerate, but give rise to drastically different free-atom (FA) orbitals.

**2.** — The question thus arises whether an LCAO calculation can actually be carried out, even starting with FA-AO's, with due account of the specific nature of those AO's. This requires taking overlap explicitly into account for s bands as well as for d bands. The mathematical aspects are known for simple cases [6] and in the general matrix LCAO formalism [7]. Unfortunately, it cannot be applied in general in the nearest neighbour approximation, because then the overlap matrix (which should be positive definite) can be either ill-behaved or singular [8] : this is likely to occur when the s-s overlap integrals between first neighbours are very large, as is the case of the iron-group metals (cf. Table II) : we have found that spurious eigenvalues of the effective one-electron Hamiltonian matrix $H$ disappear, for the s band, only when overlap up to at least 12 neighbours is taken into account. For d bands, on the other hand, inclusion of second neighbours is sufficient.

Table II

| FA config. : | d$^8$s$^2$ | | d$^9$s$^1$ | |
|---|---|---|---|---|
| Overlaps (1st and 2nd neighbours) : | | | | |
| $S_\sigma^{ss}$ | 0.449 | 0.226 | 0.518 | 0.293 |
| $S_\sigma^{dd}$ | 0.0215 | 0.0039 | 0.0324 | 0.0090 |
| $S_\pi^{dd}$ | − 0.0147 | − 0.0017 | − 0.0279 | − 0.0046 |
| $S_\pi^{dd}$ | 0.0028 | 0.0002 | 0.0064 | 0.0007 |
| Band limits (eV) : | | | | |
| s | (− 12.39 ÷ 2.91) $\alpha_s$ | | (− 25.84 ÷ 2.91) $\alpha_s$ | |
| d | (0.84 ÷ 1.31) $\alpha_d$ | | (0.69 ÷ 1.53) $\alpha_d$ | |

The bands obtained for Ni d$^8$s$^2$ and Ni d$^9$s using HF orbitals have the characteristics shown in table II. They have been calculated using an approximate quantum chemical scheme [9] especially designed for transition metals. That scheme is based on the evaluation from atomic theoretical and spectroscopic data

of the values $\alpha_s$, $\alpha_d$ of the diagonal elements of $H$ and on the approximation

$$\beta_{MN}^{(l)} \equiv H_{MN}^{(l)} = k\alpha_l(2 - |S_{MN}^{(l)}|) S_{MN}^{(l)}; \quad k = 1.75 \quad (3)$$

for the off-diagonal elements associated with atoms M and N. Equation (3), which contains the overlap $S_{MN}^{(l)}$ and a constant $k$, is a modification of Wolfsberg-Helmholtz formula, whose validity is discussed in references [10, 11]. It makes treatment of any number of neighbours possible.

Fo crystals where all sites are geometrically and chemically equivalent, equation (3) has the distinct advantage that, *under the* s-d *separation* assumption, the $\alpha$-values appear as multiplicative factors of the s and d blocks of the Hamiltonian matrix $H$.

Therefore, the application of equation (3) and the calculation of the resulting density of states $n(E)$ is straightforward, provided that the s-d blocks of $H$ and of the overlap matrix $S$ are neglected.

This assumption has been extensively used in investigations of the d-bands by the method of moments [2, 12] leading to very reasonable results. On the other hand large overlap values are not a serious difficulty in the application of that method, provided remote neighbours are taken into account to restore positive definiteness of the overlap matrix $S$. Then, even though special summing techniques are not applicable, evaluation of the traces of powers of $HS^{-1}$ will yield the successive moments.

Under the s-d separation, $H$ and $S$ commute, and the crystal orbital energies for wavevector $k$, $E_j(k)$, are simply the ratios of the corresponding eigenvalues of those two matrices. The latter eigenvalues, in turn, are simply the diagonal elements of the two matrices in the reciprocal space when also the d-d coupling is neglected [13], and can be calculated by the generalization to 12 neighbours of the well-known Koster-Slater formulas.

The DOS $n(E)$ thus obtained illustrate very effectively the dependence of $n(E)$ on the choice of the AO's. They lend further weight to studies giving a special importance to the *in situ* electron configuration of transition-metal atoms in crystals.

**3.** — We have tackled precisely the latter problem — the determination of the distribution of the valence electrons among s and d orbitals of atoms *in situ* — by referring to a model Hamiltonian of the Hubbard-SCF type. Two principles have been adopted (i), the $\alpha$-values depend on the electron population $n_\mu$ of the corresponding AO in the crystal; (ii), the Fermi levels of the s and d bands — which, we recall, are treated as separate ones in the present scheme — are equal at equilibrium.

Point (i) requires an expression for the $\alpha$'s which takes $n_\mu$ into explicit account. According to the Hubbard-SCF model for many-orbital atoms :

$$\alpha_\mu = - W_\mu + n_\mu(\mu\mu \mid \mu\mu) + \sum_{\mu' \neq \mu} n_{\mu'}(\mu'\,\mu' \mid \mu\mu) \quad (4)$$

where $W_\mu$ is an ionization potential, $\mu$ and $\mu'$ denote different orbitals of atom M; $(\mu\mu \mid \nu\nu)$ denotes an effective two-electron one-centre integral. We have chosen the parameters suggested by de Brouckère [14], with averaging of two-electron integrals over different d-orbitals and a modified $W_s$ for Co. The expressions obtained are :

$$\begin{aligned}
\text{Ni}: \quad \alpha_s &= \phantom{-}7.9181 - 8.5302\, n_s \text{ eV};\\
\alpha_d &= -4.0339 - 3.8848\, n_s \text{ eV};\\
\text{Co}: \quad \alpha_s &= \phantom{-}7.9315 - 8.0207\, n_s \text{ eV};\\
\alpha_d &= -2.2571 - 3.0213\, n_s \text{ eV};\\
\text{Fe}: \quad \alpha_s &= \phantom{-}6.7588 - 7.3690\, n_s \text{ eV};\\
\alpha_d &= -0.7813 - 2.2025\, n_s \text{ eV}; \qquad (5)
\end{aligned}$$

under the condition that $n_s + n_d = 10$, 9, 8, resp. Strictly speaking, these expressions also depend on the AO's chosen; however, since they are average values partly estimated from spectroscopic data, we shall assume that they are already an optimal choice.

Application of criterion (ii) should now yield two very important and elusive quantities : the *in situ* orbital occupation numbers and the relative positions of the d and s bands. The d-band width $W_d$, on the other hand, can serve as an indicator of quality of the approximations used. The values obtained for the group VIIIb metals in their fcc phases are shown in table III.

Table III

| | $n_s$ | $W_d$ | $E_F$-$b_s$ | $E_F$-$b_d$ | $\alpha_s$ | $\alpha_d$ |
|---|---|---|---|---|---|---|
| Ni : | 0.85 | 5.88 | 12.38 | 5.00 | 0.70 | − 7.32 |
| Co : | 0.92 | 4.87 | 11.30 | 3.70 | 0.55 | − 5.04 |
| Fe : | 0.88 | 3.23 | 7.68 | 2.21 | 0.30 | − 2.71 |

$b_s$ and $b_d$ denote the lower limits of the s and the d-band, resp..

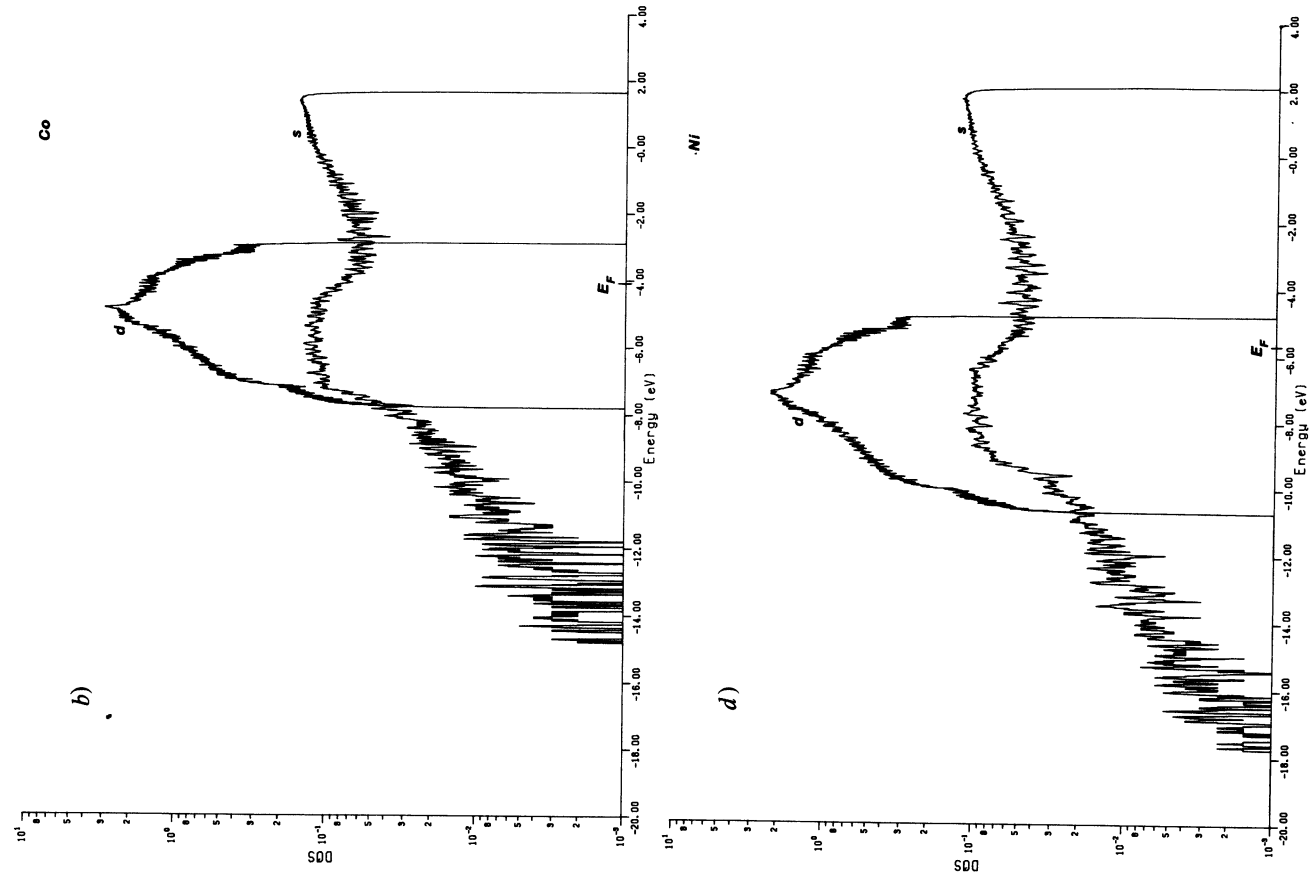
Note : The reference FA configuration has been taken with one electron on the 4s AO's. In the case of nickel, the $3d^8 4s^2$ configuration has also been used and gives

0.79 3.36 8.66 3.10 1.20 − 7.09.

These results have been discarded because, for a final 4s occupation close to one, the correct reference FA configuration is obviously the $3d^9 4s$ one.

Figure 1 presents the band-shapes obtained according to the above procedure.

From table III and the figure, it can be seen that our results are of the same order of magnitude as those of Moruzzi, Janak, and Williams (MJW) [15], obtained with the much more complicated KKR method, which is currently believed to provide the best results in as much as the density-functional formalism should take at least part of the correlation into account. Actually, the muffin-tin approximation


Co
s
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Ni
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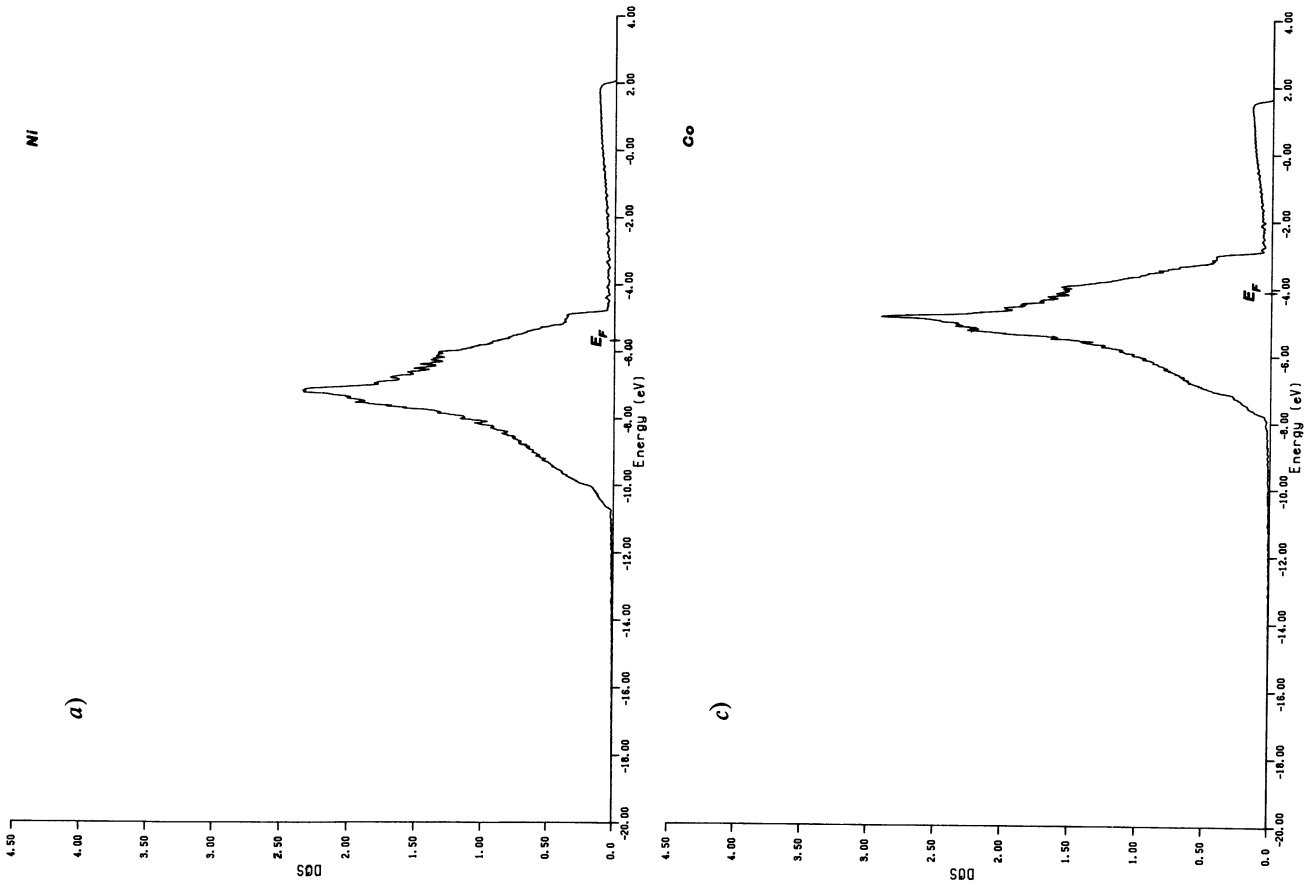
Ni
$E_F$
DOS
Energy (eV)
a)
Co
$E_F$
DOS
Energy (eV)
c)

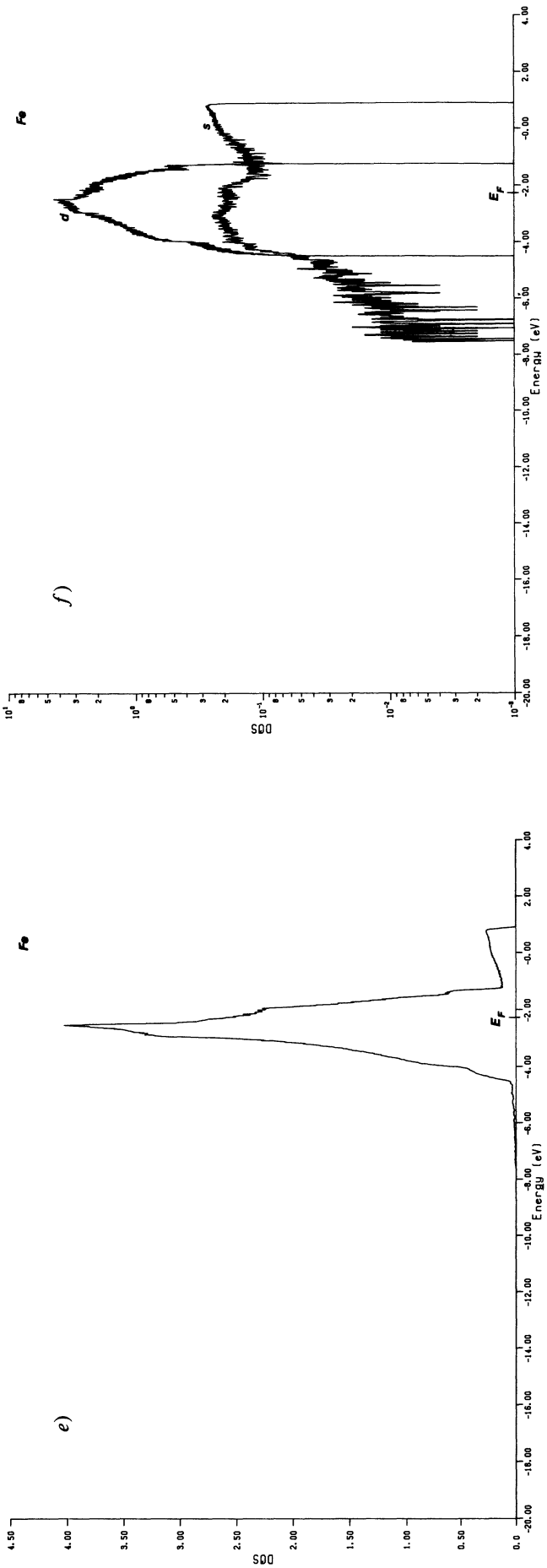


Fig. 1. — Total (self-consistent) DOS in a linear scale (a, c, e) and the constituent s- and d-DOS in a logarithmic (b, d, f) scale for fcc Ni, Co and Fe. The curves have been obtained by direct counting, in small energy intervals, of the eigenvalues calculated on a fine mesh in $k$-space (corresponding to 846 000 atoms for s-band and 389 344 atoms for d-band). The logarithmic scale allows comparison of the two bandshapes.

is a very delicate feature of the MJW procedure; nevertheless, more recent results are in accordance with them [16, 17]. The only substantial difference with respect to our results is that the widths of our bands (both occupied and unoccupied) decrease somewhat from Ni to Fe. This might be a physical effect, but it could be related as well to the fact that we have neglected d-d and s-d interactions. As concerns correlation, it should be at least partly accounted for by the very principle of Fermi-level equalization : in the molecular case, this principle would result from electro-negativity equalization, whose theoretical foundation requires a multi-configuration scheme, which in turn is a scheme including at least some degree of correlation [18].

The assessment of the physical validity of the occupation numbers obtained is not a simple task. The free-atom configurations from which our results have been obtained were all $3d^n4s$ ones. (For Ni the $d^8s^2$ configuration leads to practically the same $n_s$ value.) Table III suggests that part of the 4s electron will go into the d states : this is a well known effect resulting from bond formation (cf. e.g. [19]). It is difficult to say more about the reliability of the results, since occupation numbers are difficult to measure experimentally. For Ni, a most frequent theoretical value is $n_s = 1.2$ [20, 21]. But this value may be lower when s-d hybridization is neglected : Kleinman [20] finds in that case a value $n_s = 0.6$. Estimates of $n_s$ proposed in connection with some experimental studies are

Ni : 0.6; Co : 0.5; Fe : 1.0.

The interpolation scheme of Marshall and Bross [22], which also takes into account some experimental results, gives the value $n_s = 0.93$.

Using our self-consistent results for $\alpha$'s from table III and formula (3), we can find the values of « hopping » matrix elements $\beta$. For the d-band of Ni we have the values (in eV) :

| | dd$\sigma$ | dd$\pi$ | dd$\delta$ |
|---|---|---|---|
| 1st neighbours | − 0.82 | 0.70 | − 0.16 |
| 2nd neighbours | − 0.23 | 0.12 | − 0.02 |

They are in agreement with the values obtained by Boudeville *et al.* [23] by three-dimensional integration based on Herman-Skillman data [24]. We have checked that, in agreement with reference [23], the inclusion of second-neighbour d-d hopping elements has very little effect on the d-band width.

We conclude that even with drastic simplifications, a treatment of transition metals entirely based on the LCAO scheme and on free-atom Hartree-Fock orbitals can provide very significant results. Moreover, the combination of a technique for estimating the effective-Hamiltonian parameters from free-atom properties combined with the Fermi-level equalization condition can produce estimates of otherwise unattainable relative properties of the s- and d-states. Further work should include the removal of certain approximations and the possible inclusion of *in situ* orbital properties such as the tail damping corresponding to the RAA recipe.

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