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## Tight-binding parameters for chemisorptive bonds of transition metals with hydrogen, oxygen and sulfur

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**Résumé.** — Les paramètres de liaisons fortes ont été calculés pour les métaux de transition Fe, Co, Ni, Cu, Pd, Pt, soit pour décrire le métal pur (liaisons métal-métal), soit pour décrire un couplage avec des atomes légers, azote, carbone, hydrogène, oxygène, soufre. Pour cela, on utilise un calcul atomique self-consistent Hartree-Fock-Slater de type Herman-Skillman avec une correction de potentiel type Slater pour tenir compte des effets d'échange et corrélation. L'étude des variations des paramètres avec les distances interatomiques montre que ceux-ci décroissent exponentiellement avec la distance. Finalement les effets des intégrales de champ cristallin et des intégrales à trois centres sont discutés.

**Abstract.** — Calculations of the tight-binding parameters have been worked out for Fe, Co, Ni, Cu, Pd, Pt bonds either in metal-metal bonds or in chemisorptive bonds with oxygen, sulfur, hydrogen, nitrogen, etc. Parameters are extracted from Herman-Skillman atomic self-consistent Hartree-Fock-Slater calculations with  $\alpha$ -Schwartz correlation values. Variations of these parameters with adsorption distances are established. Surface crystal field effects and the role of three-centre integrals are discussed.

**1. Introduction.** — The most accurate way to study bulk properties of crystalline solids is to use «  $k$ -space » methods as APW or KKR in band calculations. But these methods are huge and computer time consuming. For this reason we can observe a « renaissance of the tight-binding » approach [1], less sophisticated and sufficient for investigation of qualitative properties of solids, as is the case in adsorption and catalysis field.

According to Slater and Koster's [2] ideas, the bulk properties, obtained by accurate calculations, can be adjusted in the tight-binding approximation by an interpolation scheme. So obtained, the  $dd\sigma$ ,  $dd\pi$ ,  $dd\delta$  parameters may also be used to study unrelaxed sur-

faces, kinks, holes, steps, etc., in the direct «  $R$ -space » [3]. But for an approach of surface relaxation, chemisorption, etc., they are not adapted as they are determined for a given interatomic distance.

In order to study these topics, we start the whole process by atomic calculations based on the same SCF Herman-Skillman computations as for accurate methods (Hartree-Fock-Slater Hamiltonian). We apply this method (in the same spirit as  $X_\alpha$  starting process) first to a metal atom, secondly to an adsorbed one. This permits us to obtain the same degree of approximation for adsorbate and substrate calculated atomic properties. Then we can use these results (numerical

functions) to directly build up the interatomic parameters, required to a further tight-binding approach of chemisorption.

The aim of this work is to present a study of these parameters using the tight-binding spirit where only interactions between the first nearest neighbours are considered. The way the diatomic parameters are extracted permits us to draw a parallelism between tight binding and Hückel frames and to consider with more accuracy the problem of the non-diagonal Hückel-type Hamiltonian and its lack of realism for heavy compounds. Another by-product of the algebraic attempt of parameters calculation is the great anisotropy of errors in the algebraic basis set fitting : results are good for  $\sigma$ -type multi-zeta STO integrals, poor for  $\pi$ -type and fairly bad for  $\delta$ -type interactions. So, for accurate *ab initio* angular effect calculations, we must use pure numerical functions.

**2. Parameters entering : tight binding approximation developed in heteronuclear case.** — As reviewed in many books, the tight-binding method uses the same approximation level as the one of Hückel. For this reason, as for the homonuclear case of the Hückel frame, we start by briefly considering the  $H_2^+$  bond, but we develop the formalism for the case of two different atoms A and B (Fig. 1). The Hamiltonian for the complete system will be written,  $R$  being the distance between two nuclei :

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_a} + \frac{1}{r_b} - \frac{1}{R} \right). \quad (2.1)$$

This is the correct Hamiltonian  $\hat{H} = \hat{T} + V$  for the simplest case, that of  $H_2^+$ . In a realistic case, the mono-electronic approximation leads to the same type of equation, but for the potential  $V$  we must consider

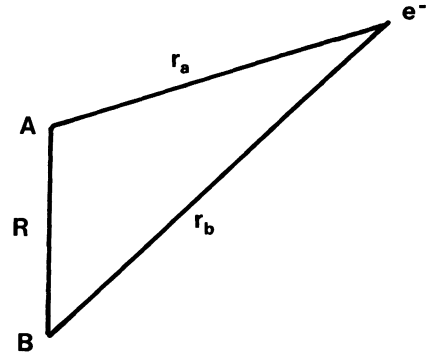


Fig. 1. — Definition of electron coordinates versus a two atoms system.

the expression derived from atomic numerical calculations :

$$V = -\frac{e^2}{4\pi\epsilon_0} \left[ \frac{f(r_a)}{r_a} + \frac{g(r_b)}{r_b} - \frac{h(R)}{R} \right] \quad (2.2)$$

where  $f, g, h$  are screening functions.

We assume that  $\psi_n$  will be satisfactorily approximated for the Schrödinger eigenvalue energy  $E_n$

$$\hat{H}\psi_n = E_n \psi_n \quad (2.3)$$

by a linear combination of atomic orbitals (LCAO) with a minimal basis set. In the case of  $H_2^+$  this gives :

$$\psi_n = C_{na} \cdot \varphi_a + C_{nb} \cdot \varphi_b \quad (2.4)$$

$\varphi_a$  and  $\varphi_b$  being atomic eigenvectors of atoms A and B associated with atomic energies  $E_a$  and  $E_b$  respectively.

Let

$$S = S_{ab} = S_{ba} = \langle \varphi_a | \varphi_b \rangle \quad (2.5)$$

be the overlap integrals.

We can then write in the simplest formalism of  $H_2^+$  :

$$\left. \begin{aligned} H_{aa} &= \langle \varphi_a | \hat{H} | \varphi_a \rangle = E_a + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_a \left| \frac{1}{r_b} \right| \varphi_a \right\rangle \\ H_{bb} &= \langle \varphi_b | \hat{H} | \varphi_b \rangle = E_b + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_b \left| \frac{1}{r_a} \right| \varphi_b \right\rangle \\ H_{ba} &= \langle \varphi_b | \hat{H} | \varphi_a \rangle = E_a \cdot S + \frac{e^2}{4\pi\epsilon_0} \frac{S}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_b \left| \frac{1}{r_b} \right| \varphi_a \right\rangle \\ H_{ab} &= \langle \varphi_a | \hat{H} | \varphi_b \rangle = E_b \cdot S + \frac{e^2}{4\pi\epsilon_0} \frac{S}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_a \left| \frac{1}{r_a} \right| \varphi_b \right\rangle \end{aligned} \right\} \quad (2.6)$$

As usual, we label  $\alpha_a$  and  $\alpha_a^b$  « crystal field integrals » (Coulomb integrals in Hückel method)

$$\alpha_a^b = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_a \left| \frac{1}{r_b} \right| \varphi_a \right\rangle \quad \text{and} \quad \alpha_a = \sum_{b \neq A} \alpha_a^b \quad (2.7)$$

and we label  $V_{ab}^a$  and  $V_{ba}^b$  « the hopping integrals » (resonance integrals in Hückel method)

$$V_{ab}^a = -\frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_a \left| \frac{1}{r_a} \right| \varphi_b \right\rangle \quad (2.8a)$$

$$V_{ba}^b = -\frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_b \left| \frac{1}{r_b} \right| \varphi_a \right\rangle \quad (2.8b)$$

and three-centre integrals :

$$V_{ab}^c = -\frac{e^2}{4\epsilon_0} \left\langle \varphi_a \left| \frac{1}{r_c} \right| \varphi_b \right\rangle. \quad (2.9)$$

Table I. —  $\alpha$  parameter values used in our calculations taken in [5a] for the elements from H to Cu and in [5b] for Pd and Pt.

Element	$\alpha$
H	0.978 04
N	0.751 97
O	0.744 47
S	0.724 75
Fe	0.711 51
Co	0.710 18
Ni	0.708 96
Cu	0.706 97
Pd	0.695 10
Pt	0.687 99

**3. Details of calculations.** — **3.1 INTRA-ATOMIC ELECTRON REARRANGEMENTS.** — The atomic wavefunctions and the potential  $V_i$  were obtained by a self-consistent atomic calculation similar to that of Herman-Skillman [4]. To take into account the exchange-correlation effects, we used the Slater local exchange-correlation potential,  $\alpha\rho^{1/3}$ , where  $\rho$  is the electronic density and  $\alpha$  is a prefactor (Table I). The prefactor  $\alpha$  is determined in the spirit of  $X_\alpha$ -method through a minimization of the difference between Hartree-Fock-Slater (HFS) and Hartree-Fock (HF) energies [5].

As we are mainly interested in catalysis by chemisorption in VI B metalloid group on metallic group VIII surfaces with defects : kinks, holes, steps, it is not possible for us to use a jellium model surface which works, for instance, with Na or Cl adatoms on simple surface of Al [6] in the spin-density functional formalism and its treatment of exchange correlation effects. Instead of employing for these effects a better formalism, as that of U. von Barth and L. Hedin, we prefer to maintain the possibility to compare our results to  $X_\alpha$  calculations on small particles (13 metallic atoms) with the same  $\alpha$ -Schwartz parameter as starting point, these  $X_\alpha$  calculations being in fact the first step in the many body problem treatment [6].

Using the above  $\alpha$ , we have performed atomic SCF calculations for Fe, Co, Ni ( $3d^8 4s^2$ ), Cu, Pd, Pt, O, S, H, Cl, C, N and stored files of numerical functions for atomic orbitals and potential on each element. For nickel, we will indicate the effect of  $\alpha$  on the value of hopping integrals. We shall also study the effect of initial configuration on the hopping integrals by comparing the atomic configurations ( $3d^8 4s^2$ ) and ( $3d^9 4s^1$ ) for Ni.

**3.2 INTER-ATOMIC ELECTRON REARRANGEMENTS.** — Therefore, such an approach leads to the following difficulty. The discrepancy between molecular and metallic situations is in the way we take into account the screening effect of the electrons on the considered electron of the monoelectronic Hamiltonian. In a non-

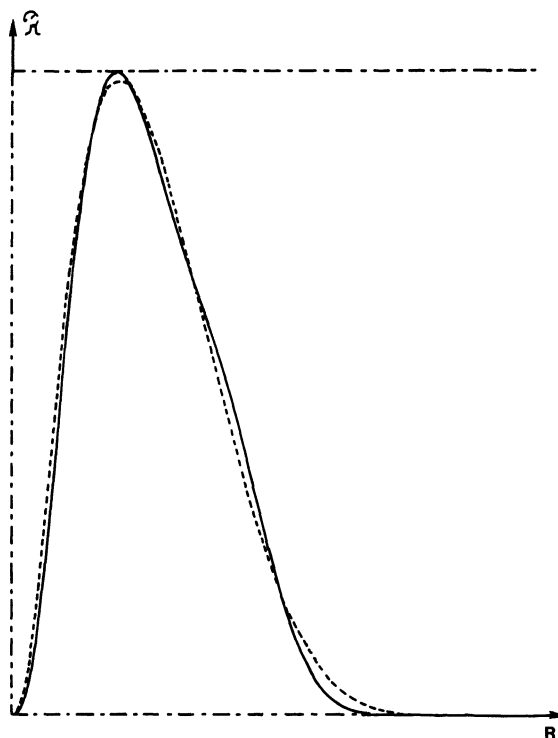


Fig. 2.1. — Radial part  $R(R)$  of the function.

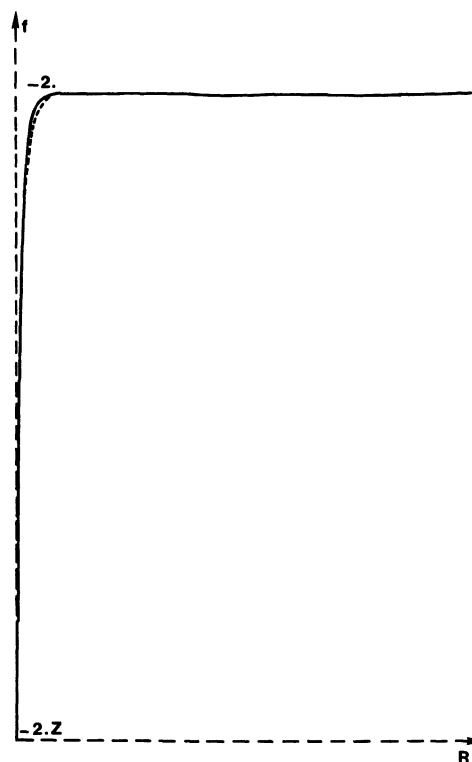


Fig. 2.2. —  $f(R) = -RV(R)$ ,  $V(R)$  being the potential.

Fig. 2. — Variation of 3d function and corresponding potential of nickel with distance  $R$ . — Dotted lines correspond to Herman-Skillman data. — Full lines correspond to multi-dzeta function and Thomas-Fermi potential of the form :  $V(R) = (-2 - 2(Z - 1) \exp(-\zeta R))/R$  with  $\zeta \simeq 3$ , if  $R$  is expressed in a.u.

metallic compound, for the molecular Hückel Hamiltonian, the formalism leads to a bare (+ 1) nucleus when the electron is removed; this corresponds to a « tail » in the Herman-Skillman potential of coulombian shape, i.e. in  $1/R$ . In the metallic case, on the other hand, a tight binding Hamiltonian takes the place of the one of Hückel and, then, the electron reorganization leads to a completely screened nucleus (equivalent to a neutral atom) at large distance. The problem is just in the definition of this cut off in long range properties.

In the present work, we have made the following approximations :

a) If a nucleus bears an orbital function, the involved part of the structure is considered as *intra-molecular* and affected by the electron described by the mono-electronic Hamiltonian; for that reason the potential is chosen exactly as the Herman-Skillman potential (with tail of coulombian shape). It looks like a Thomas-Fermi potential (Fig. 2.2).

b) If a nucleus bears no orbital function, the involved part of structure is considered as *inter-molecular* and we assume that the electron reorganization is complete on this nucleus. The potential is a solution of Poisson's equation and, for that reason, has no long range effect (characterized by an  $1/R$  long range shape). As the electronic density on this nucleus vanishes, the potential also vanishes.

To focus on our parameters problem this means that the hopping integrals  $V_{ab}^a$  will be calculated with a potential of  $1/R$  long range shape and the crystal field or three-centre integrals without this  $1/R$  tail. In the homonuclear case in which only « d-orbitals » are involved we shall use for hopping integrals  $V_{ab}^a$  the usual notation  $dd\lambda$  with :  $\lambda = \sigma, \pi, \delta$  according to the symmetry of the bond.

**4. Algebraic calculations for diatomic parameters.** — In the initial part of our work, we have represented

Table II. — *Algebraic radial part of 5d platinum orbital corresponding to*

$$\mathcal{R}_{5d}(R) = \sum_{n=3}^5 \sum_{i=1}^2 c_{in} (2 \zeta_{in})^{n+1/2} [(2n)!]^{-1/2} \times \\ \times R^{n-1} e^{-\zeta_{in} R}$$

$n$	$i$	$c$	$\zeta$
3	1	0.338 63	18.539
	2	0.003 631 3	31.161
4	1	− 0.409 10	9.068 2
	2	− 0.216 87	21.304
5	1	0.679 12	2.524 3
	2	0.594 96	5.639 4

our numerical wavefunctions by a sum of Slater multi-dzeta functions orthonormalized by Schmidt's method. Like Gaussian-Type Orbitals (GTO), we considered that, more than pure numerical ones, Slater-Type Orbitals (STO) were easier to handle. So, the optimization of the platinum 5d functions required first the fitting of 3d functions to extract 3d

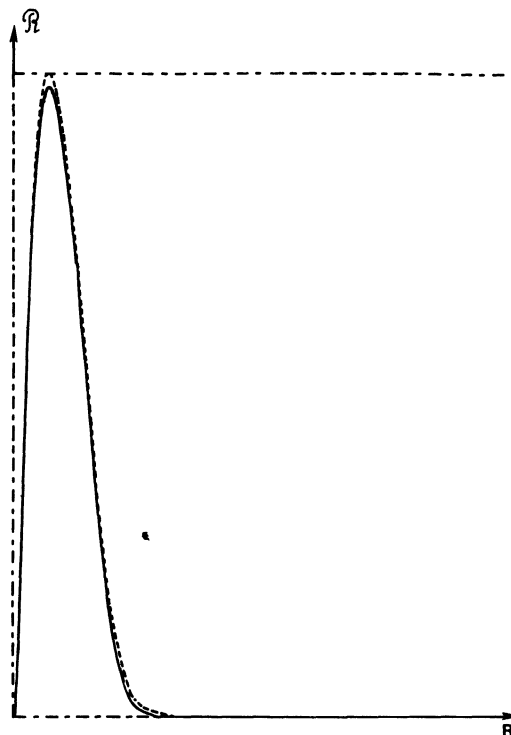


Fig. 3.1. — Corresponds to 3d function.

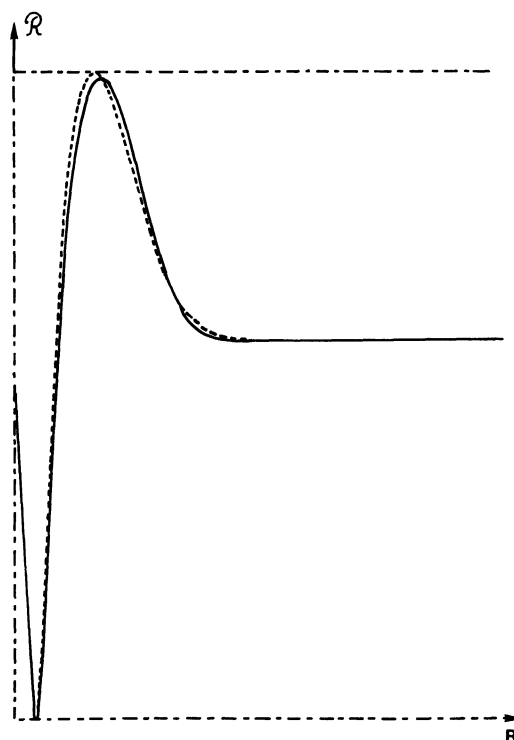


Fig. 3.2. — Corresponds to 4d function.

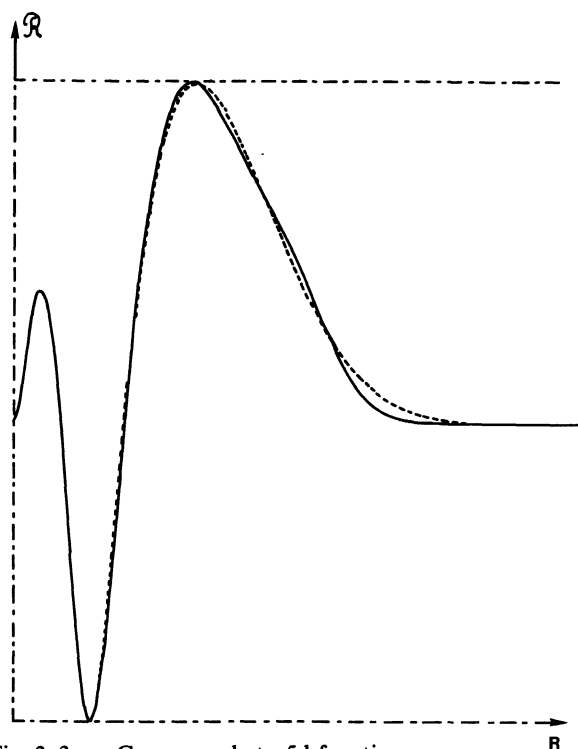


Fig. 3.3. — Corresponds to 5d function.

Fig. 3. — Variation of radial part  $R$  of  $nd$  functions of platinum with distance  $R$ . — Dotted lines : Herman-Skillman functions. — Full lines : multi-dzeta functions. The HS functions are expressed in the form  $R_{nd}(R) = aR_n(c, R) + bR_n(d, R)$  with  $R_n(\zeta, R) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} R^{n-1} e^{-\zeta R}$ .

algebraic parameters, then the 4d and finally the 5d ones (Table II). The fitting of numerical functions by algebraic functions is excellent (see Fig. 2.1 and 3) and the behaviour of core functions is perfect. The Herman-Skillman potential can be well fitted (the derivative discontinuation included) by a Thomas-Fermi potential (Fig. 2.2). In the best known case, i.e. for nickel, we see (Table III.1) that the Herman-Skillman wave functions are diffuse compared to those of Clementi and close to those of Richardson which are the most suitable functions of quantum chemistry [7-9] for the first transition series atoms.

Looking at the column describing  $\sigma$ -type parameters of nickel  $3d^8 4s^2$  (Table III.2), we see the extreme sensitivity of the  $dd\sigma$  parameter to the wave function shape and to the choice of the potential. The multi-dzeta Clementi wave functions (very contracted) lead to parameters which are much too weak. The best agreement with the interpolation scheme data is given by the H.S. fitted function using a Thomas-Fermi optimized potential for the  $3d^8 4s^2$  configuration. The  $3d^9 4s^1$  configuration (Table V) leads to much larger parameters for Ni-Ni bond. This is in agreement with the results of Snow and Waber [10] who studied the influence of the initial atomic configuration on various sets of APW energy

bands calculations. Thus, for nickel, we shall use the usual atomic configuration  $3d^8 4s^2$  (Table IV).

Table III. — Calculations corresponding to nickel S.T.O.

A : Clementi functions.

B : Richardson functions.

C : Optimized functions.

D : Non-optimized functions.

E : Similar to C but with a Thomas-Fermi potential.

F : Results obtained from interpolation schemes [3, 20].

1 : Algebraic radial part of the 3d nickel orbital corresponding to

$$R_{3d}(R) = \sum_{i=1}^2 c_i (2\zeta_i)^{7/2} [6!]^{-1/2} R^2 e^{-\zeta_i R}$$

	$C_1$	$C_2$	$\zeta_1$	$\zeta_2$
A	0.421 20	0.706 58	6.705 55	2.873 81
B	0.568 3	0.629 2	5.75	2.
C	0.611 23	0.563 498	5.676 9	2.139 5
D	0.579 47	0.594 73	6.088 4	2.301 4
E = C	0.611 23	0.563 498	5.676 9	2.139 5

2 : Hopping integrals  $dd\sigma$ ,  $dd\pi$ ,  $dd\delta$  between two nickel atoms at a distance of 2.492 Å from each other.

	$dd\sigma$	$dd\pi$	$dd\delta$
A	− 0.009 8	0.003 3	− 0.000 33
B	− 0.047 1	0.028 1	− 0.004 6
C	− 0.031 6	0.016 6	− 0.002 5
D	− 0.025 7	0.012 1	− 0.001 6
E	− 0.043 8	0.027 5	− 0.005 33
F	− 0.041 7	0.018 8	− 0.002 3

Table IV. — Configurations used in our calculations.

Fe	$3d^6 4s^2$
Co	$3d^7 4s^2$
Ni	$3d^8 4s^2$
Cu	$3d^{10} 4s^1$
Pd	$4d^{10}$
Pt	$5d^9 6s^1$

Beside the potential, if one chooses to replace the numerical HF SCF functions by the best choice of algebraic multi-Slater orbitals (*a fortiori* gaussian-type orbitals), the « round-off » error on tails is huge and the diatomic parameters (platinum  $dd\delta$  for instance) vary from  $-0.013\ 3$  Ryd. for the numerical function to  $-0.006\ 6$  Ryd. for the best algebraic one (Table VI).

When the tight-binding parameters  $dd\sigma$ ,  $dd\pi$ ,

$dd\delta$  are deduced from interpolation schemes, they may be considered as independent of each other. In our case, the three parameters are connected and only dependent on the ratio between the range of the considered orbitals and the distance  $R$  of the bond. The way our parameters vary with distance allows us to study them at some distances between adsorbate and metal and for different crystal faces. As we have pointed out in a previous short report about nickel [12],

Table V. — *Values of nickel integrals.*

A : Usual configuration  $3d^8\ 4s^2$  with  $\alpha = 0.708\ 96$ .

B : Configuration  $3d^9\ 4s^1$ .

C : Usual configuration with  $\alpha = 1$ .

D : Integrals obtained from band structure [12, 20].

1 : Hopping integrals  $dd\sigma$ ,  $dd\pi$ ,  $dd\delta$  and overlap integrals  $S\sigma$ ,  $S\pi$ ,  $S\delta$  between two nickel atoms at a distance of  $2.492\ \text{\AA}$  from each other.

	$dd\sigma$	$dd\pi$	$dd\delta$	$S\sigma$	$S\pi$	$S\delta$
A	$-0.043\ 8$	$0.027\ 5$	$-0.005\ 33$	$0.026\ 4$	$-0.022\ 4$	$0.005\ 45$
B	$-0.054\ 2$	$0.042\ 5$	$-0.010\ 6$	$0.033\ 7$	$-0.038\ 3$	$0.012\ 6$
C	$-0.034\ 3$	$0.018\ 2$	$-0.002\ 97$			
D	$-0.041\ 7$	$0.018\ 8$	$-0.002\ 33$			

2 : Overlap integrals  $S$  and hopping integrals  $V$  between a  $3d$  function of a nickel atom and  $s$  and  $p$  functions of H, O and S atoms.

The notations are the same as in table III.

Orbital on X	$R$	Type of bond	Configuration	$S_{Ni-X}$	$V_{Ni-X}^{Ni}$	$V_{X-Ni}^X$
H 1s	1.86	$\sigma$	A	0.100	$-0.141$	$-0.168$
			B	0.133	$-0.153$	$-0.226$
O 2s	2.08	$\sigma$	A	0.073 7	$-0.077\ 5$	$-0.157$
			B	0.103	$-0.090\ 6$	$-0.229$
O 2p		$\sigma$	A	$-0.070\ 8$	0.122	0.131
			B	$-0.079\ 6$	0.124	0.157
		$\pi$	A	0.049 7	$-0.058\ 3$	$-0.065\ 3$
			B	0.069 3	$-0.066\ 5$	$-0.095\ 2$
S 3s	2.28	$\sigma$	A	0.072 8	$-0.086\ 4$	$-0.119$
			B	0.103	$-0.096\ 9$	$-0.174$
S 3p		$\sigma$	A	$-0.077\ 5$	0.136	0.118
			B	$-0.088\ 4$	0.139	0.143
		$\pi$	A	0.061 2	$-0.072\ 6$	$-0.061\ 9$
			B	0.088 0	$-0.083\ 2$	$-0.092\ 3$

the ratios of integrals  $|dd\sigma/dd\pi|$  and  $dd\sigma/dd\delta$  approach those determined by Heine [11] using the resonance theory. The choice of  $\alpha$ , coefficient of the exchange term of  $X_{\alpha}$ , by influencing the atomic orbital range, leads to a good agreement when the Schwartz value [5] is used for  $\alpha$ , while the value  $\alpha = 1$  contracts the orbital too much. This decrease of the band-width when increasing the exchange potential is in agreement with band calculations of Ni of Connolly [13] which show the same effect.

**5. Numerical calculations of integrals. Their accuracy.** — Figure 2.3 shows, for platinum, the excellent result of optimization process between the Herman-Skillman 5d numerical function and the 6-dzeta algebraic representation of the same function (Table II). Both are orthogonalized to the core (3d and 4d) and are like each other in this range. However, this is not the case for the binding range and the tail of the 5d function. The two bumps of the main lobe of the algebraic function are unavoidable and due to the fact that the function is performed by the two outermost STO of quantum number  $n = 5$  in this area, while the numerical 5d Herman-Skillman function is smooth and does not show such sign changes of the second derivative. Table VI illustrates the effect of this fitting and optimization of multi-dzeta functions on the parameter values.  $dd\sigma$  decreases only by 25 % with use of algebraic functions, while the directional character of  $\pi$  (at 45° from the bond, displacing the major integration area in the tail region) and chiefly of  $\delta$  (at 90° from the bond line) leads to a decrease of 34 % for  $dd\pi$  and of 50 % for  $dd\delta$ , which is unacceptable. This is due to the fact that, for  $\delta$  bonds, the maxima of the wave function amplitude are parallel to each other and perpendicular to the bond line, and thus the inadequate representation of tails plays a very important part. This shows that an algebraic integration of multi-dzeta cannot lead to acceptable values of the parameters.

For this reason, we had to leave the usual approach of binding parameters (in extended Hückel frame) which consists in the use of Slater multi-exponential algebraic wave functions and Thomas-Fermi potentials. We performed a purely numerical development in calculation of these integrals.

For non-modification of Herman-Skillman numerical functions within their non-linear scale (the ratio of arithmetical series doubling each 40 points) we have performed a quadratic approach of functions on three next nearest neighbours of a considered Gauss point. The three dimensional integration (in  $\rho, \theta, \varphi$ ) has been obtained by a double-quadrature Gauss-Legendre method in elliptical coordinates ( $\lambda, \mu$ ) assuming  $\varphi$ -cylindrical symmetry. For  $V_{ab}^a, V_{ba}^b$  (i.e.  $dd\lambda$ ) 64 points have been taken for each coordinate, i.e.  $64 \times 64 = 4096$  points for the whole quadrature. To obtain an equivalent cost for a non-symmetric case, we have considered 16 Gauss-Legendre points

for each ( $\lambda, \mu, \varphi$ ) coordinate, which leads to a 1 % precision and is quite sufficient. We have been able to test the precision of a double numerical integration on the example of  $dd\sigma, dd\pi$  and  $dd\delta$  parameters for Pt-Pt bond (Table VI).

Table VI. — Values of hopping integrals between 5d functions on two platinum atoms separated by a distance of 2.772 Å.

A : Non-relativistic APW parameters [16, 20].

E : Herman-Skillman +  $\alpha V_{\text{exch}}$  parameters obtained from numerical integration.

F : Parameters obtained from STO fitted on HS and numerically integrated.

C : Parameters obtained from STO fitted on HS and algebraically integrated.

The perfect agreement obtained between F and C (about  $6 \times 10^{-3}$ ) is a test of our method of numerical integration. This has allowed us to use it in the E case for which an algebraic integration could not be considered. The E case (Herman-Skillman +  $\alpha V_{\text{exch}}$ ) is that which leads to the best values of the ratios  $|dd\sigma/dd\pi|$  and  $dd\sigma/dd\delta$ , in principle, respectively, equal to 1.5 and 6 [11].

	$dd\sigma$	$dd\pi$	$dd\delta$	$ dd\sigma/dd\pi $	$dd\sigma/dd\delta$
A	− 0.058 7	0.023 3	− 0.002 4	2.52	24.5
E	− 0.096 8	0.064 8	− 0.013 3	1.49	7.3
F	− 0.072 5	0.042 2	− 0.006 6	1.71	11.0
C	− 0.072 4	0.042 4	− 0.006 6		

While the algebraic function is an approximation of the Pt-5d orbitals, the representation of this 5d-algebraic function by a numerical function on the non-linear Herman-Skillman scale does not lead to any loss of precision ( $< 10^{-6}$ ). Then, we have calculated the integrals both by an algebraic method for the algebraic 5d orbital (multi-dzeta Slater orbitals and Thomas-Fermi potential) and a numerical method for the numerical representation of the same functions (elliptic coordinates). The worse result (Table VI) corresponds to a  $6 \times 10^{-3}$  precision, that is sufficient for qualitative parameters.

**6. Results and discussion.** — Our calculated integrals are collected in tables VII to XI. In figures 4 to 7, we show the variation of parameters with distance, which is the only variable in the calculations. This is a way of solving the uncertainties in adsorption distance corresponding to the different crystal faces. For the metal-metal Pt-Pt bonds, the calculated ratios  $|dd\sigma/dd\pi|$  and  $dd\sigma/dd\delta$  are of the order of 1.5 and 7 in accordance with those based on reso-



Table VII. — Values of hopping and overlap integrals between two metal atoms calculated from wave functions and potentials obtained in a calculation  $H.S. + \alpha V_{\text{exch}}$ .  $R$  (Å) represents the distance between two atoms (equilibrium distance in the bulk of metal);  $dd\sigma$ ,  $dd\pi$  and  $dd\delta$  (Ryd) represent hopping integrals between d functions;  $S\sigma$ ,  $S\pi$ ,  $S\delta$  are corresponding overlap integrals.

	$R$	$dd\sigma$	$dd\pi$	$dd\delta$	$S\sigma$	$S\pi$	$S\delta$
Fe 3d	2.482	− 0.062 4	0.042 7	− 0.009 03	0.037 1	− 0.035 5	0.009 66
Co 3d	2.506	− 0.050 5	0.032 8	− 0.006 58	0.030 7	− 0.027 3	0.006 94
Ni 3d	2.492	− 0.043 8	0.027 5	− 0.005 33	0.026 4	− 0.022 4	0.005 45
Cu 3d	2.556	− 0.042 8	0.031 9	− 0.007 48	0.027 9	− 0.029 4	0.008 97
Pd 4d	2.751	− 0.080 1	0.062 8	− 0.015 5	0.057 7	− 0.065 3	0.020 9
Pt 5d	2.772	− 0.096 8	0.064 8	− 0.013 3	0.067 1	− 0.062 1	0.016 1

nance theory [11] and our previous results on nickel [12]. Two main ideas can be pointed out :

First, the  $T_{\mu\nu}$  term of the extra-diagonal elements  $H_{\mu\nu}$  of the Hamiltonian must not be neglected. The fact can be explained this way : the hermiticity of the Hamiltonian gives  $H_{\mu\nu} = H_{\nu\mu}^*$ . But for the potential term  $V_{\mu\nu} = \beta_{ab}$  and  $V_{\nu\mu} = \beta_{ba}^*$ , in the Pt-O bond for instance, the two terms differ from each other by as much as a factor of two; this means that  $T_{\mu\nu}$  must not be neglected. It is impossible to weigh the  $\beta$  terms by  $\beta_{ab}^* = \frac{1}{2}(\beta_{ab} + \beta_{ba})$  because the bond is too dissymmetric. The formula :

$$(E_a - E_b) \cdot S_{ab} = V_{ab}^a - V_{ba}^b \quad (6.1)$$

is a practical way to handle this asymmetry (Table IX).

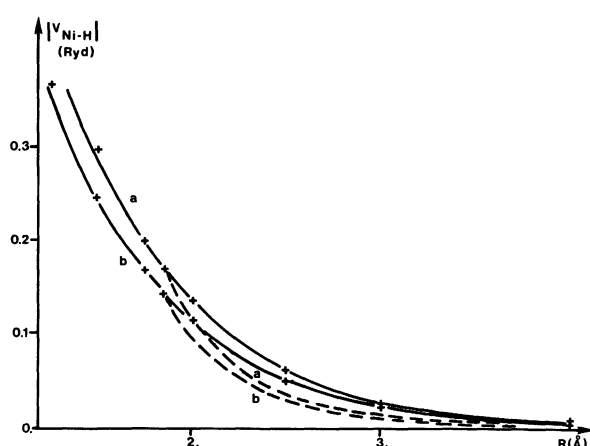


Fig. 4. — Variation of hopping integrals  $V_{\text{Ni-H}}$  between nickel and hydrogen with interatomic distance  $R$  (Å). + Represent calculated points. — Dotted lines correspond to a  $R^{-5}$  fitting. — Full lines correspond to a  $\exp(-\lambda(R - R_0)/R_0)$  fitting (here the value is  $\lambda = 2.92$  for  $R_0 = 2.492$ ). (a) curves represent  $V_{\text{H-Ni}}^{\text{H}}$  integrals; (b) curves represent  $V_{\text{Ni-H}}^{\text{Ni}}$  integrals.

The second idea to formulate is the inadequacy of the various approximations relating  $H_{\mu\nu}$  to the direct overlap  $S_{\mu\nu}$  for transition metal compounds such as the Wohlsberg-Helmholtz one :

$$H_{\mu\nu} = \frac{k}{2} S_{\mu\nu} (H_{\mu\mu} + H_{\nu\nu}) \quad (6.2a)$$

or that of Longuet-Higgins and Roberts :

$$H_{\mu\nu} = k S_{\mu\nu} \quad (6.2b)$$

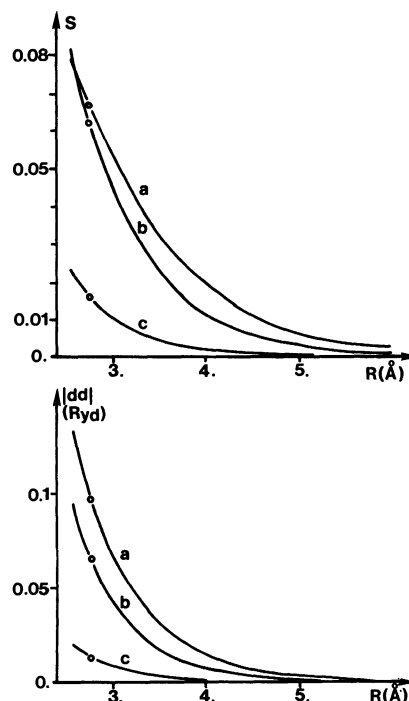


Fig. 5. — Comparison between variations of overlap integrals  $S$  and hopping integrals  $|dd\lambda|$  between two platinum 5d functions with interatomic distance  $R$  (Å). o correspond to usual distance  $R_0 = 2.772$  Å. (a) curves correspond to  $\sigma$  bond; (b) curves correspond to  $\pi$  bond; (c) curves correspond to  $\delta$  bond.

Table VIII. — Integrals calculated from  $HS + \alpha V_{\text{exch}}$  functions and potentials.

$S_{AB}$  : is the overlap integral  $\langle \varphi_A | \varphi_B \rangle$ ;  
 $V_{AB}^A$  : is the hopping integral corresponding to a potential centred on A atom :  $\langle \varphi_A | V_A | \varphi_B \rangle$ ;  
 $V_{BA}^B$  : is the hopping integral corresponding to a potential centred on B atom :  $\langle \varphi_B | V_B | \varphi_A \rangle$ ;  
 $R$  : is the distance between A and B atoms. This distance has been chosen from values concerning complexes found in the literature.

Orbital on A	Orbital on B	Type of bond	R	$S_{AB}$	$V_{AB}^A$	$V_{BA}^B$
Fe 3d	H 1s	$\sigma$	1.81	0.131	-0.176	- 0.227
	O 2s	$\sigma$	2.15	0.0856	-0.0804	- 0.182
	2p	$\sigma$		-0.0786	0.124	0.143
	$\pi$	0.0568		-0.0595	- 0.0740	
	S 3s	$\sigma$	2.44	0.0780	-0.0757	-0.122
	3p	$\sigma$		-0.0843	0.126	0.118
	$\pi$	0.0636		-0.0645	-0.0611	
Co 3d	H 1s	$\sigma$	1.67	0.131	-0.202	-0.247
	O 2s	$\sigma$	2.12	0.0784	-0.0777	-0.167
	2p	$\sigma$		-0.0741	0.122	0.136
	$\pi$	0.0524		-0.0581	-0.0684	
	S 3s	$\sigma$	2.33	0.0775	-0.0841	-0.125
	3p	$\sigma$		-0.0820	0.136	0.122
	$\pi$	0.0646		-0.0719	-0.0644	
Ni 3d	H 1s	$\sigma$	1.86	0.100	-0.141	-0.168
	O 2s	$\sigma$	2.08	0.0737	-0.0775	-0.157
	2p	$\sigma$		-0.0708	0.122	0.131
	$\pi$	0.0497		-0.0583	-0.0653	
	S 3s	$\sigma$	2.28	0.0728	-0.0864	-0.119
	3p	$\sigma$		-0.0775	0.136	0.118
	$\pi$	0.0612		-0.0726	-0.0619	
Cu 3d	H 1s	$\sigma$	1.46	0.158	-0.250	-0.338
	O 2s	$\sigma$	2.20	0.0796	-0.0655	-0.170
	2p	$\sigma$		-0.0680	0.0965	0.122
	$\pi$	0.0523		-0.0481	-0.0679	
	S 3s	$\sigma$	2.31	0.0900	-0.0852	-0.149
	3p	$\sigma$		-0.0817	0.127	0.128
	$\pi$	0.0760		-0.0731	-0.0782	
Pd 4d	H 1s	$\sigma$	2.04	0.177	- 0.176	- 0.219
	O 2s	$\sigma$	2.01	0.171	- 0.157	- 0.396
	2p	$\sigma$		- 0.118	0.199	0.255
	$\pi$	0.117		- 0.114	- 0.168	
	S 3s	$\sigma$	2.32	0.153	- 0.136	- 0.259
	3p	$\sigma$		- 0.125	0.189	0.204
	$\pi$	0.130		- 0.115	- 0.136	
Pt 5d	H 1s	$\sigma$	2.06	0.170	- 0.192	- 0.265
	O 2s	$\sigma$	2.02	0.167	- 0.173	- 0.381
	2p	$\sigma$		- 0.132	0.237	0.278
	$\pi$	0.113		- 0.125	- 0.160	
	S 3s	$\sigma$	2.31	0.148	- 0.153	- 0.249
	3p	$\sigma$		- 0.138	0.228	0.221
	$\pi$	0.124		- 0.129	- 0.129	

or that of Ballhausen and Gray :

$$H_{\mu\nu} = kS_{\mu\nu}[H_{\mu\mu} \cdot H_{\nu\nu}]^{1/2}. \quad (6.2c)$$

The extra-diagonal term  $H_{\mu\nu}$  is directly linked to  $V_{\mu\nu}$ . The approach of the  $V_{\mu\nu}$  term by a formula proportional to  $S_{\mu\nu}$  leads to an inaccurate binding effect (the bond is a consequence of  $H_{\mu\nu}$ ). For instance, for the Pt-Pt bond integrals *versus*  $R$ , the inter-atomic distance, the curves  $S_{dd\sigma}$  and  $S_{dd\pi}$  cross one another while the  $V_{dd\sigma}$  and  $V_{dd\pi}$  curves are quite parallel around the binding distance (Fig. 5). We can show the same discrepancy between  $S_{\mu\nu}$  and  $V_{\mu\nu}$  when we study variations on the row Fe, Co, Ni, Cu (Fig. 8) or on the column Ni, Pd, Pt (Fig. 9). There is no similarity between curves.

The examination of Ni-H curves *versus* the bond distance  $R$ , as well as other curves function of adsorption distance, shows that (Table XII, Fig. 4) the variations of hopping integrals, which mostly contribute to the chemical bond, are not in  $R^{-5}$  as conjectured by the resonance theory [11] but rather in  $e^{-qR}$  [17]. So we have obtained a good agreement between the exponential law and the parameter variation with distance. It leads to a very simple way of obtaining, with two points on a curve, parameters for all the adsorption distances on crystal faces and reaction paths.

**7. Further developments.** — The method used in this paper leads to some approximations we wish to point out here :

*First*, in the heteronuclear case, we have shown that the empirical Hamiltonian conventionally developed on an atomic-orbital basis set leads to a non-hermitian matrix. For instance, in the case of the bond between

iron and oxygen, the parameters are linked to the « usual Hamiltonian » by :

$$H_{ab} = \beta_{ab} = V_{ab}^a = -0.0804 \text{ Ryd.} \quad (7.1a)$$

$$H_{ba} = \beta_{ba} = V_{ba}^b = -0.182 \text{ Ryd.} \quad (7.1b)$$

We prefer to assign the approximation to the whole Hamiltonian taking into account the hermiticity property, explicitly. For such empirical non-diagonal elements, the relation  $H_{\mu\nu} = H_{\nu\mu}$  implies the equation (6.1) :

$$(E_a - E_b) \cdot S_{ab} = V_{ab}^a - V_{ba}^b.$$

In the expression of  $H_{\mu\nu}$  let us define

$$\Delta_{ab}^* = (V_{ab}^a - V_{ba}^b) \cdot S_{ab}^{-1}. \quad (7.2)$$

If we replace atomic energy levels  $E_a$  and  $E_b$  by

$$E_a^* = \frac{E_a + E_b}{2} + \frac{\Delta_{ab}^*}{2}; \quad E_b^* = \frac{E_a + E_b}{2} - \frac{\Delta_{ab}^*}{2} \quad (7.3)$$

the hermiticity condition (6.1) will be automatically satisfied. We can then remark that the error due to this substitution is within approximation of the whole method. For instance, for the FeO bond (in which  $V_{Fe,O}^{Fe}$  and  $V_{O,Fe}^O$  are in ratio of 1 to 2), we are led to the values

$$E_{Fe}^*(3d) = -0.5436$$

instead of

$$E_{Fe}(3d) = -0.5439 \text{ Ryd.},$$

$$E_O^*(2s) = -1.7345$$

instead of

$$E_O(2s) = -1.7322 \text{ Ryd.}$$

Table IX. — Comparison between  $(E_{Pt} - E_X) \cdot S_{Pt-X}$  and  $V_{Pt-X}^{Pt} - V_{X-Pt}^X$ . Notations used are the same as in table VIII.  $E_{Pt}$  and  $E_X$  are the energy levels obtained for the corresponding orbitals.

Orbital on X	Type of bond	$R$	$S_{Pt-X}$	$V_{Pt-X}^{Pt}$	$V_{X-Pt}^X$	$(E_{Pt} - E_X) S_{Pt-X}$	$V_{Pt-X}^{Pt} - V_{X-Pt}^X$
H 1s	$\sigma$	2.06	0.170	-0.192	-0.265	0.017	0.073
N 2s 2p	$\sigma$	2.01	0.183	-0.206	-0.361	0.157	0.155
	$\sigma$		-0.138	0.266	0.281	-0.004	-0.015
	$\pi$		0.136	-0.156	-0.174	0.004	0.018
O 2s 2p	$\sigma$	2.02	0.167	-0.173	-0.381	0.208	0.208
	$\sigma$		-0.132	0.237	0.278	-0.023	-0.041
	$\pi$		0.113	-0.125	-0.160	0.019	0.035
S 3s 3p	$\sigma$	2.31	0.148	-0.153	-0.249	0.109	0.096
	$\sigma$		-0.138	0.228	0.221	0.0007	0.006
	$\pi$		0.124	-0.129	-0.129	-0.0006	0.

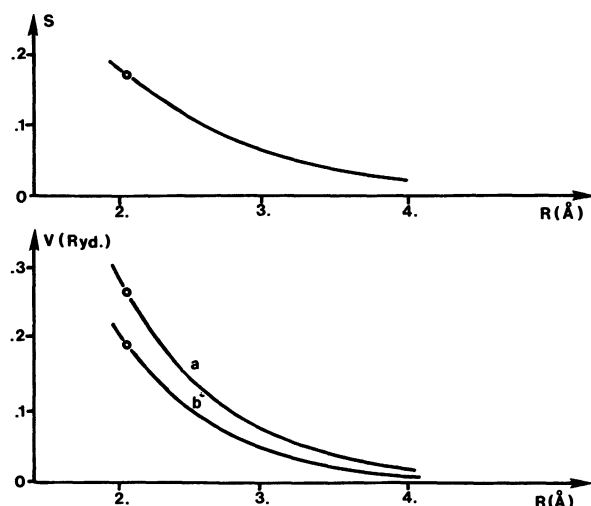


Fig. 6. — Comparison between variations of overlap integral  $S$  and hopping integrals  $V$  between a 5d function of platinum and a 1s function of hydrogen with interatomic distance  $R$ .  $\circ$  corresponds to distance  $R_0 = 2.06$  Å. (a) curve corresponds to  $V_{H-Pt}^H$  integrals; (b) curve corresponds to  $V_{Pt-H}^{Pt}$  integrals.

The important point to notify here is the necessity to add the non-diagonal kinetic term, dependent on the values of  $E_a^*$ ,  $E_b^*$  and  $S_{ab}$ , to the formulation commonly used  $H_{ab} = \beta_{ab}$ , even in the recent tight binding bulk method calculations [1, 11].

Then we propose to use  $E_a^*$  and  $E_b^*$  deduced from formulae in the  $H_{\mu\nu}$  formulation because the relative corrections  $E_a^* - E_b^*$  of  $E_a - E_b$  will be very weak (they can be extracted from table IX), even when  $V_{ab}^a$  and  $V_{ba}^b$  are in a ratio of 1 to 2 as in the Fe-O bond.

We want to mention here the imprecision inherent to data extracted from atomic hydrogen calculations. The hydrogen data are the least precise because, in this case, when the atom is involved in a molecule, one electron is replaced by two, which leads to the biggest exchange-correlation potential change. The atomic orbitals, atomic energies and electron correlations are the least accurate. The best treatment would be to use, instead of atomic data, those issued from bi-nuclear molecular SCF process, by recalculation, on this basis, of atomic-like properties.

Second, the atomic orbitals do not constitute an orthogonalized basis set (OAO). For instance, in

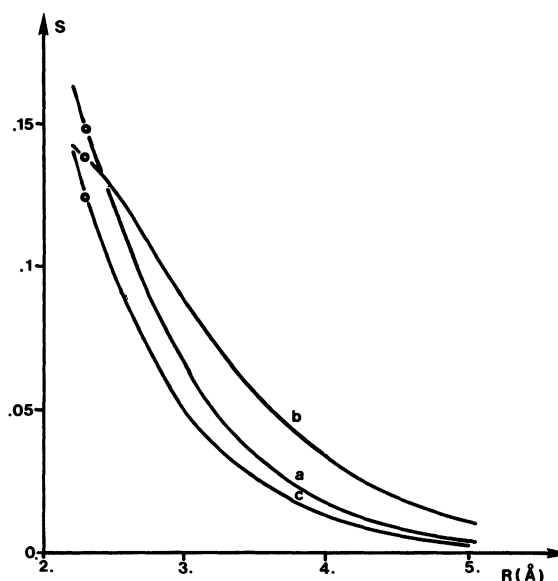


Fig. 7.1. — Comparison between variation of overlap integrals  $S$  between a 5d function of platinum and a function of sulfur with interatomic distance  $R$  (Å).  $\circ$  corresponds to a distance  $R_0 = 2.31$  Å. (a) curve corresponds to a  $\sigma$  bond and a 3s function for  $S$ ; (b) curve corresponds to a  $\sigma$  bond and a 3p function for  $S$ ; (c) curve corresponds to a  $\pi$  bond and a 3p function for  $S$ .

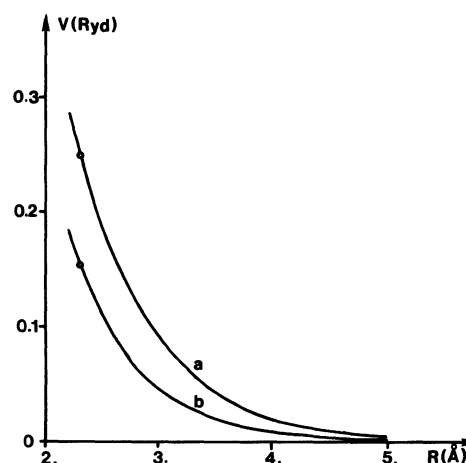


Fig. 7.2. — Comparison between variations of hopping integrals  $V$  between a 5d function of platinum and a 3s function of sulfur with interatomic distance  $R$  (Å).  $\circ$  corresponds to a distance  $R_0 = 2.31$  Å; (a) curve corresponds to  $V_{S-Pt}^S$  integrals; (b) curve corresponds to  $V_{Pt-S}^{Pt}$  integrals.

Table X. — Values of crystal field integrals  $V_{AA}^B$  and three centre integrals  $V_{AB}^C$ . The inter-atomic distances are 2.492 Å for nickel and 2.772 Å for platinum.

	$V_{AA}^B(\sigma)$	$V_{AA}^B(\pi)$	$V_{AA}^B(\delta)$	$V_{AB}^C(\sigma)$	$V_{AB}^C(\pi)$	$V_{AB}^C(\delta)$
Ni	− 0.012	− 0.003	0.007	− 0.013	0.014	− 0.004
Pt	− 0.035	− 0.005	0.013	− 0.030	0.039	− 0.011 3

the bond between platinum and oxygen, the overlap  $S_{ab}$  is 0.167 and we should have to employ the Löwdin method  $\psi_A = \hat{S}^{-1/2} \Phi_A$  to use orthonormal atomic orbitals instead of crude atomic ones as we do. Another way is to extend the continued fraction expansion formalism often used [2] to describe the chemisorption process to take into account this effect.

Third, there are the « atomic relativistic effects ». The Mattheiss platinum calculations, as our parameters calculations, for comparison purpose, start from the non-relativistic Herman-Skillman method. Qualitatively, one of the effects of using the atomic Dirac calculations instead of the Schrödinger equation is often the contraction of numerical atomic orbitals. As we have done on platinum surface atoms [15] it is possible to take into account spin-orbit coupling on the atomic basis using the  $\xi$ -parameter of Herman-Skillman tables [4, 15, 16]. But the effect on the radial part of 5d orbital is small enough to be neglected for our calculations. On the other hand, the chemisorption problem necessitates the description of s orbitals and the 6s relativistic contraction [18]

is 20 %. For this reason, when platinum is involved in a bond by its 6s orbitals, the relativistic effects should be fully considered.

**8. Anisotropic crystal field integrals.** — In the same way as we have defined in part 1 integrals  $V_{dl\lambda}^{(A,B)}$  and  $V_{dl\lambda}^{(A,B)}$  which were established by purely numerical calculations (« round-off » error  $< 6 \times 10^{-3}$ ), we can use the same approach to calculate crystal-field integrals  $\alpha_{ll}$  (notation defined by Fig. 10)

$$\alpha_{ll} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{R} - \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_l \left| \frac{1}{\rho} \right| \varphi_l \right\rangle. \quad (8.1)$$

We shall now discuss the anisotropic character of the so-called « crystal field integrals » without focusing too much on the formalism problems

$$\begin{aligned} \frac{1}{\rho} &= \frac{1}{R} \left[ \sum_{k=0}^{\infty} \left( \frac{r}{R} \right)^k P_k(\cos \theta) \right] = \\ &= \frac{1}{R} \left[ 1 + \sum_{k=1}^{\infty} \frac{r^k}{R^k} P_k(\cos \theta) \right] \end{aligned} \quad (8.2)$$

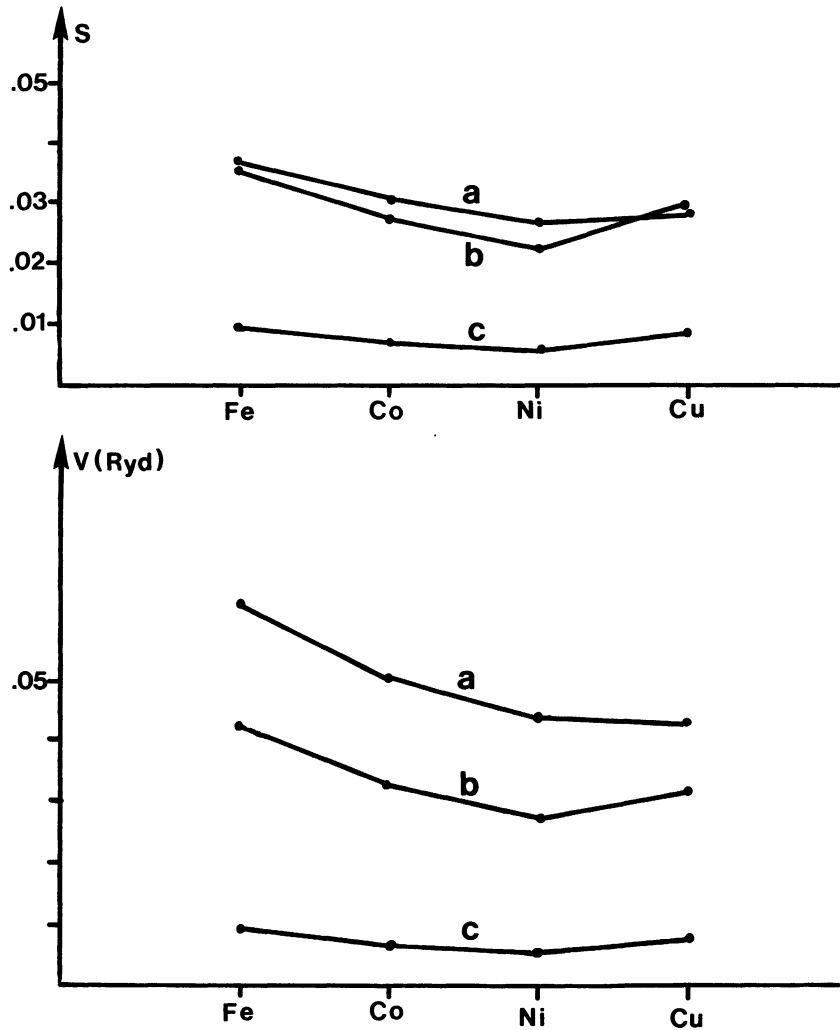
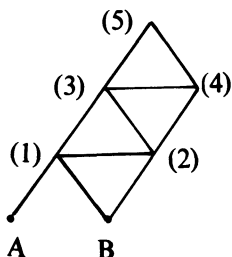


Fig. 8. — Variations of overlap integrals  $S_s$ ,  $S_\pi$ ,  $S_\delta$  (Fig. 8.1) and of hopping integrals  $V_s$ ,  $V_\pi$ ,  $V_\delta$  (Fig. 8.2) between 3d functions with the considered element (first transition row) for usual interatomic distances : 2.482 Å for Fe, 2.506 Å for Co, 2.492 Å for Ni, 2.556 Å for Cu.

Table XI. — Variation of three centre  $\sigma$  integrals of platinum with the position of the third atom C.

C position	$ V_{AB}^C(\sigma) $
(1)	0.030 0
(2)	0.019 1
(3)	0.014 1
(4)	0.011 2
(5)	0.009 2



and

$$\alpha_{II} = \frac{e^2}{4\pi\epsilon_0} \times \left\langle \varphi_I \left| \sum_{k=1}^{\infty} \frac{r^k}{R^{k+1}} P_k(\cos \theta) \right| \varphi_I \right\rangle. \quad (8.3)$$

Table XII. — Expression of the formulae of the fitting of some hopping integrals with the inter-atomic distance  $R$ . They lead to a very good agreement with calculated points.

$V_{Ni-Ni}(\sigma)$	$-0.0437 \exp(-4.7(R-2.49)/2.49)$
$V_{H-Ni}^H$	$-0.168 \exp(-2.92(R-1.86)/1.86)$
$V_{Ni-H}^{Ni}$	$-0.141 \exp(-2.92(R-1.86)/1.86)$
$V_{Pt-Pt}(\sigma)$	$-0.097 \exp(-4.23(R-2.77)/2.77)$
$V_{Pt-Pt}(\pi)$	$0.065 \exp(-4.97(R-2.77)/2.77)$
$V_{Pt-Pt}(\delta)$	$-0.013 \exp(-5.54(R-2.77)/2.77)$
$V_{H-Pt}^H$	$-0.265 \exp(-2.82(R-2.06)/2.06)$
$V_{Pt-H}^{Pt}$	$-0.192 \exp(-2.96(R-2.06)/2.06)$

This well-known formula in crystal field theory leads by a straightforward calculation to selection rules on  $\langle Y_{l_1}^{m_1} | Y_{l_2}^{m_2} | Y_{l_3}^{m_3} \rangle$  that limit the series to a few terms [19] with even parity in  $I_2/R^3$  and  $I_4/R^5$  for d-orbitals. This is exactly the crystal field development in ionic compounds which gives rise to the anisotropic effects as we can see on computed values.

The first term (in  $1/R$ ), cancelled, corresponds to the Madelung constant, that is to say an isotropic term. It has, for that reason, nothing to do with « crystal field » effects. It shifts down all the orbitals and corresponds to the electrostatic interaction potential of all the nuclei. Examination of table X shows that « crystal field » integrals are very small for the bulk of metal. « Directional effects » compensate each other with the high symmetry of the lattice point group  $O_h$ . The splitting  $\Delta(t_{2g} - e_g)$  is 0.008 5 Ryd. On the opposite side, close to the metallic surface, the high symmetry is destroyed and the maximal splitting is multiplied by the factor 2.35 for (100) plane.

The results of figure 11 show the importance of anisotropic « crystal field effects » close to surfaces.

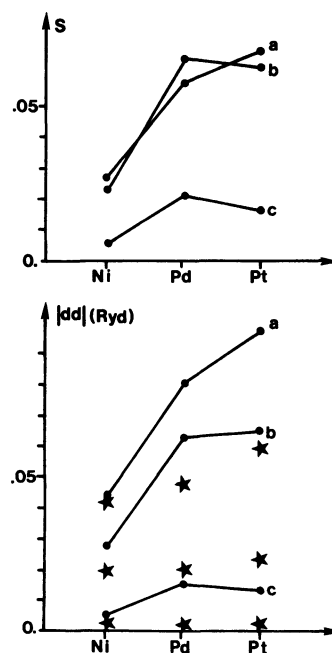


Fig. 9. — Comparison between variations of overlap integrals  $S$  and hopping integrals  $|dd|$  between two  $nd$  functions of metal atoms with the number of  $d$  row for usual interatomic distances : 2.452 Å for Ni, 2.751 Å for Pd, 2.772 Å for Pt. \* correspond to usual values obtained from interpolation schemes. (a) curves correspond to  $\sigma$  bonds; (b) curves correspond to  $\pi$  bonds; (c) curves correspond to  $\delta$  bonds.

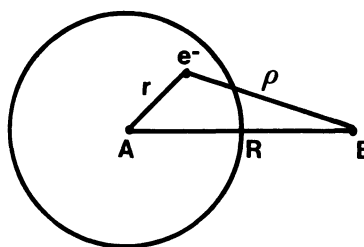


Fig. 10. — Definition of coordinates of an electron in a Wigner-Seitz cell corresponding to an atom A bound to another atom B.

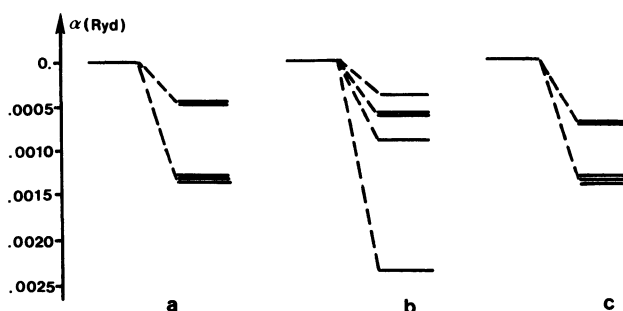


Fig. 11. — Shift of  $d$  levels of Ni obtained from calculation of  $V_{AA}^B$  integrals. (a) In the bulk; (b) On the (100) face; (c) On the (111) face.

Three-centre integrals (Tables X and XI) have weak values and furthermore, as for crystal field integrals, the first order of the value  $V_{ab}^c$  is compen-

sated by the term  $\frac{e^2}{4\pi\epsilon_0} \cdot \frac{S_{ab}}{R}$  which leads to an overall totally negligible effect.

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