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Resonant Descriptions of Bonding and Reactivity of Group VIII–IB Metals in the Solid State

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1 Introduction

Approximately three-quarters of all elements are metals; those in group VIII–IB are of very great importance in heterogeneous catalysis. Here we consider their bonding in the solid state and the effect that this has on their reactivity, adsorptive, and catalytic properties.

Resonance[1,2] was developed [3] for conjugated organic molecules,[4] but was always difficult to examine on the grounds that the individual valence bond structures do not have an existence[5] which could be isolated and subjected to experimental investigation. However, recent calculations[6] have suggested that a resonant valence bond model of benzene may be more suitable than previously supposed. Nevertheless, some electron states in benzene and naphthalene are delocalized over the entire molecule; thus both localized and delocalized approaches are required.

Quasi one-dimensional *organic* solids with conjugation[7] have received much attention as prototype polymers which might in principle exhibit metallic conduction [*e.g.* polyacetylene, polyparaphenylene, poly(phenylene)sulphide, polythiophenes, polypyrrole, *etc.*].[8] In all these cases p_z–p_z overlap (after formation of C–C σ backbones from sp^2–sp^2 overlap) produces the relevant π and π^* orbitals. Thus *cis-* and *trans*-polyacetylene[9]

and

without defects would show extensive π-electron delocalization and a conduction band half-filled with p_z electrons whose energies may be calculated assuming a one-dimensional box of electron delocalization along the chains ($E_z = n^2h^2/8mL_z^2$,

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[1] L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, 1960.

[2] C. K. Ingold, *Nature*, 1938, **141**, 314.

[3] J. C. Slater, *Phys. Rev.*, 1931, **37**, 481; L. Pauling, *J. Am. Chem. Soc.*, 1931, **53**, 1367, 3225; L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 988, 3570; E. Huckel, *Z. Phys.*, 1931, **70**, 204; 1931, **72**, 310; 1932, **76**, 628; 1933, **83**, 632.

[4] L. Pauling and J. Sherman, *J. Chem. Phys.*, 1933, **1**, 606.

[5] L. H. Long's translation of Huckel's 'Structural Chemistry of Inorganic Compounds', Vol. 1, Elsevier, New York, 1950, last paragraph.

[6] P. L. Cooper, J. Gerratt, and M. Raimondi, *Nature*, 1986, **327**, 699.

[7] M. R. Bryce and L. C. Murphy, *Nature*, 1984, **309**, 119.

[8] R. H. Friend, D. C. Bott, D. D. C. Bradley, C. K. Chai, W. J. Feast, P. J. S. Foot, J. R. M. Giles, M. E. Horton, C. H. Pereira, and P. D. Townsend, *Philos. Trans. R. Soc.*, 1985, **314**, 37; R. J. Gillespie and P. Day (ed.), *Philos. Trans. R. Soc. London Ser. A.*, 1985, **314**, 1—198; G. Harbeke, D. Baeriswyl, H. Kiess, and W. Kobel, *Phys. Scr.*, 1986, **T13**, 302.

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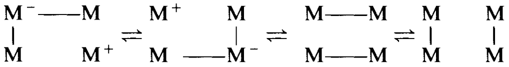
where L_z is the length of the chain of electron delocalization in the z direction and n is the number of filled states). E_z decreases as L_z increases. Naturally, this is the ground-state situation and thermal excitation would modify the fraction of electrons in the π^* states.

However, distortions[10] (*i.e.* solitons or mobile neutral point-defects) are known to exist in such conjugated organic solids which limit L[11] and reduce potential metallic conductivity to semiconductivity or insulator properties.[12] Indeed the filled π and unfilled π^* states are separated by 1.4 eV in real *trans*-$(CH)_x$ whose conductivity *rises* with increasing temperature[9] (unlike a metal). Nevertheless, $(CH)_x$ conductivity can be raised significantly by doping to produce partial oxidation or reduction, in which case the soliton defects carrying net positive or negative charges [*i.e.* $(CH^{y+})_n$ polycarbonium or $(CH^{y-})_n$ polycarbanion species exist] with the impurity electron states sitting midway between the energies of the π and π^* states.[12] Such delocalization and π-bonding can certainly exist over *two dimensions* (*e.g.* graphite[13]) and *three dimensions* (*e.g.* C_{60} carbon clusters with icosahedral symmetry[14]).

2 Metal–Metal Bonding

A similar situation exists with metal–metal bonding. Pauling[15] proposed that unsynchronized resonances of metal–metal covalent hybrid bonds existed such that covalent bonds moved from one M—M pair to another, with the result that the electronic charge on the M atoms was not identical. Thus one half of the metal atoms can be thought of as having zero charge, but one quarter will have unit positive charge and the remaining quarter will have unit negative charge. Thus, these can be represented as a mixture of



$$\begin{array}{ccccccccccccccc} M^- & \text{---} & M & & M^+ & & M & & M & \text{---} & M & & M & & M \\ | & & & \rightleftharpoons & & & | & \rightleftharpoons & & & & \rightleftharpoons & | & & | \\ M & & M^+ & & M & \text{---} & M^- & & M & \text{---} & M & & M & & M \end{array}$$

with a wandering resonant orbital (*i.e.* the metallic orbital) which is normally unfilled. *It is this which defines the reactivity and characteristic properties of the metal.* This resonating valence-bond concept of metals (and alloys) has been compared with Kekulé structures[16] of aromatic molecules.[17]

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[13] R. L. Brown and S. E. Stein, *Proc. Inst. Conf. Coal. Sci.*, IEA, 1983, p. 461.

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[17] L. Pauling, *Proc. R. Soc. London, Ser. A.*, 1949, **196**, 343.

A relationship must exist between the bonding in molecules and complexes and solid-state surface chemistry;[18] so extending the bonding concepts of molecules to the realm of the metallic solid-state may be profitable. Metal–metal bonds in complexes and clusters have been well reviewed.[19] Multiple metal–metal bonds exist in metal dimers in the vapour state, metal carbonyls, carboxylate salts, and crystalline halides[2,3,20–22] and even quadruple metal–metal bonds have long been known.[23] Furthermore, there appears to be a similarity between the reactivity of metal–metal double and triple bonds and those of alkenes and alkynes.[24] Carbon–carbon double and triple bonds are $(\sigma)^2(\pi)^2(\pi^*)^0(\sigma^*)^0$ and $(\sigma)^2(\pi)^4(\pi^*)^0(\sigma^*)^0$, but multiple metal–metal bonds may be derived from σ, π, and δ bonding [*e.g.* W≣W quadruple bonds[25] may be $(\sigma)^2(\pi)^4(\delta)^2$-$(\delta^*)^0(\pi^*)^0(\sigma^*)^0$].

The bonding which may contribute to metal–metal interactions in group VIII–IB metals is shown in Figure 1 as *non*-hybridized orbitals. First, because as Figure 2 shows the $(n)d$-states (especially at the right-hand side of the transition metal rows) are energetically far removed from the $(n)p$ and $(n + 1)p$ atomic states, thereby minimizing *d–p* overlap. The *f* and *g* states will be similarly far away in energetic terms.[27] Second, because the $(n + 1)s$ atomic orbital which is energetically much closer will not so greatly affect the spatial geometry of the *s–d* hybrid orbitals. It is of course recognized that octahedral Pt^{4+} (*e.g.* in $PtCl_6{}^{2-}$) exhibits d^2sp^3 hybrid orbitals probably because it has moved from the zero-valent Pt back four points to the left of Figure 2 with the result that *s–p–d* energies are now very much closer. Therefore descriptions in Figure 1 are appropriate to zero-valent group VIII–IB metals, but *d–s–p hybrid* orbitals are more important for positive oxidation states of these metals and metals to the left in the Periodic Table. Although *d*-orbitals alone are not good for bonding [and have been classified as (i) bonding and (ii) non-bonding[28]] they do provide the majority of the directional properties of the orbitals

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[18] J. K. Burdett, *Progr. Solid. State Chem.*, 1985, **15**, 173; J. W. Lauher, *J. Am. Chem. Soc.*, 1979, **101**, 2604; N. D. S. Canning and R. J. Madix, *J. Phys. Chem.*, 1984, **88**, 2437; E. L. Muetterties, *Science*, 1977, **196**, 839; E. L. Muetterties, *Angew. Chem.*, 1978, **17**, 545; E. L. Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.

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[25] E. M. Larson, T. M. Brown, and R. B. Von Dreele, *Acta Crystallogr.*, 1986, **42B**, 533.

[26] W. Hume-Rothery 'Atomic Theory for Students of Metallurgy', Institute of Metals, 1960, p. 386; R. Latter, *Phys. Rev.*, 1955, **99**, 510.

[27] L. Pauling, *Proc. Natl. Acad. Sci U.S.A.*, 1977, **74**, 5235.

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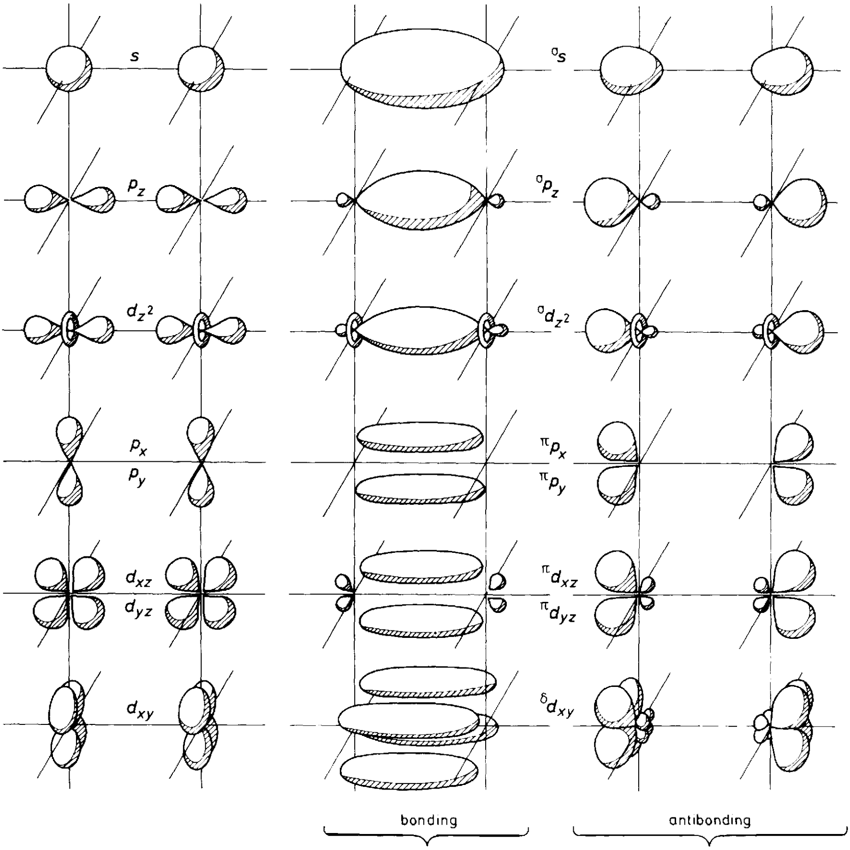

Figure 1 *Interactions of group* VIII, n(d), *or* IB, (n + 1)s, *atomic orbitals contributing to metal–metal bonding.*[19] *In theory, nine hybrid orbitals are available* [i.e. (n)d + (n + 1)s + (n + 1)p] *but since both filled* (n)p *and unfilled* (n + 1)p *states have rather different energies from the filling* (n)d *state in Figure* 2 *their contribution to hybrid orbitals of* nd *states is judged marginal, especially at the right-hand side of the zero-valent transition elements* (i.e. *group* VIII). *The effect of the energetically closer* (n + 1)s *orbital on the observed spatial geometry of the hybrid* $(n)_d$ *orbital is small. Overlap of* $d_{x^2-y^2}$ *orbitals will also produce* δ *orbitals*

irrespective to the *s* and *p* contribution. Metal–metal bonds between group VIII and IB metals may thus involve formation of $(\sigma)(\pi)_2(\delta)_2(\delta^*)_2(\pi^*)_2(\sigma^*)$ molecular orbitals of increasing energy.

The highest occupied MO (HOMO) at 0 K is given by $E = n.^2h^2/8mL^2$ for a one-dimensional box of dimension L, with n filled or partially filled MO states; as L

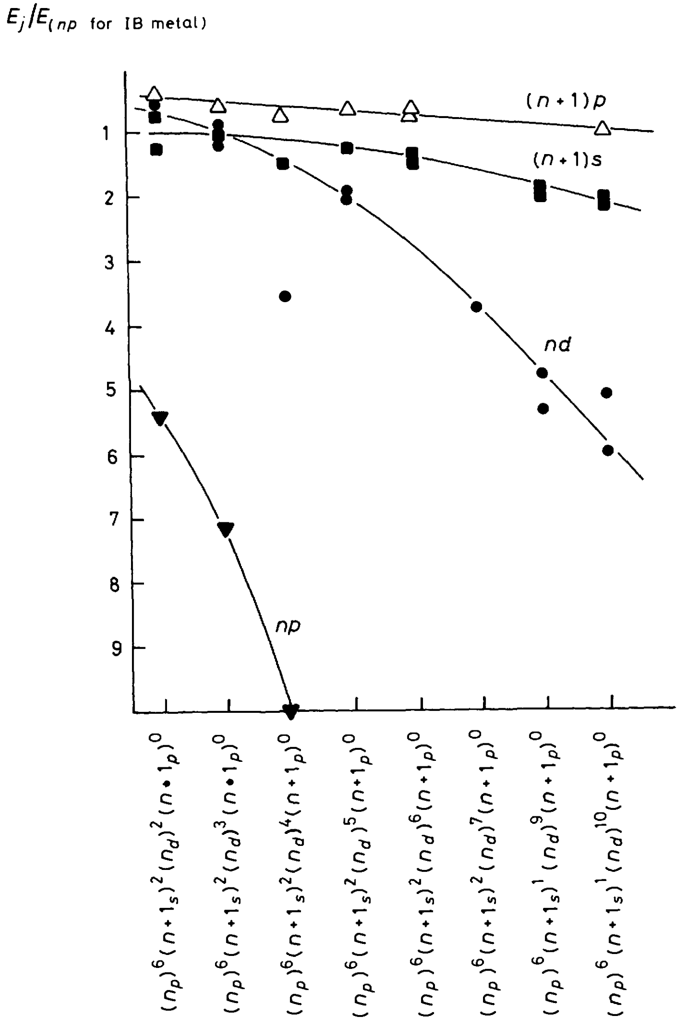

Figure 2 *Energies of filled or filling* (n)p (▼), (n)d (●), (n + 1)s (■) *and unfilled* (n + 1)p (△) *orbitals for transition metals of the first, second, and third series* (i.e. *when* n = 3, 4, *and* 5) *relative to the* (n + 1)p *orbital energy for the relevant* IB *metal during filling of the* (n)d *orbital. These are calculated from the Thomas–Fermi–Dirac potential.*[26] *Therefore as* d-*orbital filling occurs so hybridization becomes less likely*[26]

increases so E decreases and this may be differentiated with respect to energy E to give a density of states plot where $\mathrm{d}n/\mathrm{d}E$ is proportional to $E^{1/2}$. The extent of electron excitation rises with increasing T but here consideration is given to metallic bonding for group VIII and IB metals in the *ground-state situation*, when these are *in one-dimensional chains, in two-dimensional surfaces, and in the three-dimensional solid state, and how this controls the stability and reactivity of such metallic states.*

A metal is that which has a significant fraction of mobile electrons and an ability to form positive positive ions; in the former context we were long ago reminded that it was possible to prepare a composite metallic substance from non-metallic constituent elements,[29] and especially at high pressure.[29] In addition Dowden[30] has commented that the situation at metal surfaces is essentially the same as that met in unsaturated organic molecules with a resonating bond system. The rationale behind the development of the valence bond resonant model for metals[2,15] and the basis this had in organic chemistry is therefore clear.

A. One-Dimensional Metal–Metal Bonding.—Just as quasi-one-dimensional *organic* solids can exhibit conductivities similar to metals, especially when modified by partial oxidation, so can $K_2Pt(CN)_4Br_x.3H_2O$; this is a metallic conductor along the Pt–Pt–Pt chains at room temperature.[31] Hexagonal or tetragonal Rh^I-bis-diisocyanobiphenyl polymers can also be prepared using 4,4′-diisocyanobiphenyl ligands with a one-dimensional metal conduction band between $Rh^+\cdots Rh^+\cdots Rh^+$ centres in D_{4h} symmetry at distances of 0.34—0.35 nm.[32] These are one-dimensional conductors since conductivity between metal columns (0.9—1.5 nm apart) is minimal. The properties of these one-dimensional conductors have been described in terms of d_{z^2} and p_z overlap (and to a lesser extent d_{xy} and d_{yz} overlap).[33] If the metal atoms come close enough[34] in the z-direction then conductivity decreases in the sequence $z \gg x,y$ and in the z-axis a metallic bond is formed through the whole crystal, or at least until the next defect dislocating the metal–metal chain; *i.e.* translational misalignment between the laminae will clearly disrupt one-dimensional conductivity.

Bonding in the above Pt^{2+} and $Rh^+ d^8$ complexes with columns of coordinated metal ions involves[33] $M_{d_{xy}} \rightarrow CN_{2\pi^*}$ and $CN_{5\sigma^*} \rightarrow M_{d_{x^2-y^2}}$ overlaps in the xy

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[33] K. Krogmann, *Angew. Chem.*, 1969, **8**, 35.

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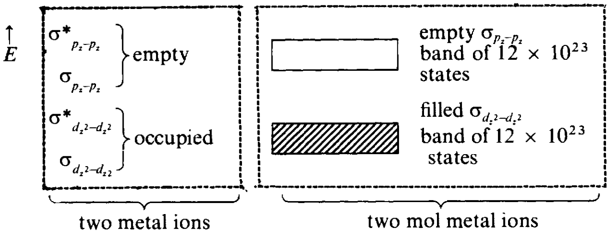
planes (perpendicular to the metal–metal columns), but p_z–p_z and d_{z^2}–d_{z^2} overlap within the metal ion columns produces the following states of decreasing energy:



Conductivity remains very low within the chains containing filled $\sigma_{d_{z^2}-d_{z^2}}$ and empty $\sigma_{p_z-p_z}$ states unless partial oxidation or reduction changes electron occupancy. Then, as the number of Pt^{2+}—Pt^{2+} or Rh^{+}—Rh^{+} centres involved increases we move to a band of these states. Such delocalization of orbitals in organometallic compounds has been compared to those in organic compounds and metals[35] (despite possible involvement of *dsp* hybridization[36] in metal–metal interactions therein, rather than the simple *d–d* overlaps). Nonetheless it is certainly true that *d* and *p* orbitals will define in large part the spatial geometry of such ligand orbitals. Others have considered similar situations in $Mg[Pt(CN)_4].7H_2O$[37] and Rh^{2+} and Ir^{+} columnar stacking complexes[38] where distances between chains can also be very large (*e.g.* 1—2 nm) but distances between metal atoms along the chains are quite short (*e.g.* 0.3 nm). In Ir^{+} and Rh^{+} the *d*-states may be spread outwards further than in Pt^{2+} complexes.

Pauling's resonating valence bond theory of metals (RVBM) has been used[39] to describe bonding along the chains in such solid complexes of d^8 metal ions where columns are associated with Pt^{2+}–Pt^{2+} interactions. RVBM assigns metallic radii (R_n) and metal–metal bond distances (D_n) such that

$$R_n = R_0 - 0.300\,(\log n)$$
$$D_n = D_0 - 0.600\,(\log n)$$

where R_0 and D_0 are values when the bond order n is 1 (*i.e.* for the single metal–metal bond). Thus as the metal–metal bond order increases so the metallic radii and metal–metal bond separations decrease. The RVBM assumes that resonating states

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[35] R. E. Rundle, *J. Phys. Chem.*, 1957, **61**, 45.

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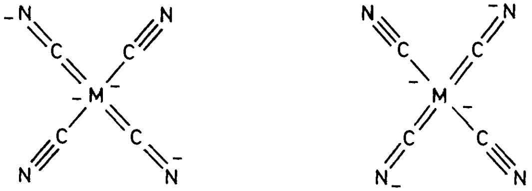
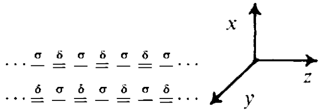
exist within the chains. Pt^{2+} and Rh^{+} are in a low-spin state with two electrons in a bonding a_{1g} state and two in an antibonding a_{2u} state. Therefore this is a non-bonding situation, but degenerate orbitals of the same symmetry repel each other and a partial bond is formed. If a_{2u} electrons are partially removed then bond order increases and metal–metal distances decrease. The resonances within the *x*–*y* plane with CN^- ligands may be represented as



where there may be advantages of *trans*-ligands moving into analogous resonance structures in unison. Since the in-plane CN ligands are good σ-donors and π-acceptors, the electron density at the d^8 metal ions might be modified. Metal–metal bonding perpendicular in the *z* axis may *also* involve resonance; such bonding results in a largely filled $\sigma_{d_{z^2}-d_{z^2}}$ band, composed of equal numbers of $(\sigma_{d_{z^2}-d_{z^2}})$ and $(\sigma^*_{d_{z^2}-d_{z^2}})$ states, and a largely unfilled σ_{p_z} band. Fractional electron removal from metal d_{xy} states by the π-acceptor ligands in the *xy* plane may well allow δ bonding along the *z*-chain from d_{xy}–d_{xy} overlap or add to the σ_{p_z} state and encourage $\sigma_{p_z-p_z}$ bonding, *i.e.* we have weak metal–metal bonding which exists between alternating pairs of d^8 metal ions:



(see Figure 3)

and so we have limited resonance along the *z*-axis with bonds of a low order and lengths of about 0.3 nm. This situation will undoubtedly form a weakly conjugated system (*i.e.*· · · σ—δ—σ—δ· · ·) which can be described by two resonant structures of a delocalized state over significant distances. The resonating valence bond model suggests that in the Rh^{+}—Rh^{+} chains there may be 0.3 metallic orbitals: the Rh—CN interactions within the *x*—*y* laminae could produce the varying metal oxidation state associated with unsynchronized resonances along the one-dimensional metal—metal chains in the *z*-axis. Both approaches are therefore complementary. Such a description of bonding without substantial *dsp* hybridization is, as we have seen, most appropriate for group VIII transition metals in a low oxidation. It would not be appropriate for earlier transition metals.

B. Two-dimensional Metal–Metal Bonding.—Approaches have been made to relate the bonding within transition metal complexes and clusters to those at transition metal surfaces.[40] However, with zero-valent metal surfaces we must now be dealing, at least on the right-hand side of the transition metal series, with a reduced extent of *d–s–p* hybridization. Balazs and Johnson used SCF-X_α-SW molecular orbital calculations of 10 atom Pt clusters and 5 atom Pt clusters as models of Pt(100) and steps in higher index planes respectively. The 10-atom cluster was a model for the (100) face of Pt, where the central surface Pt atom had its nearest-neighbour surface atoms and the entire ensemble had C_{4v} symmetry. UPS of Pt(100) shows a sharp peak at 0.25 eV below the E_f[41] and this may be attributable to an unsaturated dangling bond sticking out perpendicular to the surface. However, would associated adjacent dangling-bonds be sensed and differentiated by UPS? Thus it is not surprising that the contour of the d_{xy} contribution to the HOMO may correspond to a net *antibonding interaction* (as would be expected for the top of the band). Since this band has no lobes sticking out of the (100) surface it will presumably not contribute to adsorption and catalysis thereon. Such orbitals were judged relatively localized on the relevant metal atoms. Calculations[40] suggest that electron density is located preferentially *at the corners*, which is where surface scientists would *expect greatest reactivity*. If we turn our attention to the d_{yz} and $d_z{}^2$ orbitals, these are now directed perpendicularly out from the surface (as surface dangling bonds) and they were judged to be involved in defining activity of the (100) face in chemisorption and catalysis (*i.e.* as HOMOs they can donate charge to H_2 antibonding orbitals as predicted[42] from photoemission studies). The $d_z{}^2$ orbital has been particularly involved in σ-bonding with *symmetry conserving* orbitals of impinging reactants; others[43] have suggested that the $d_z{}^2$ orbital is the most important for chemisorption on the surface. If a diatomic molecule impinges collinearly-perpendicular with the surface above a surface atom then it has been thought that it will mix its σ and σ^* orbitals with the d_{yz} and d_{xz} orbitals of the metal; if it is collinear with the *z* direction then it will mix its σ_z and $\sigma_z{}^*$ orbitals with the $d_z{}^2$ metal orbitals.[44] Clearly antibonding interactions of a surface atom with underlying bulk atoms produces lobes which extend further from the surface and into vacuum. They assumed that dangling surface bonds (or coordinatively unsaturated atoms) are even more prevalent at edges and steps, although Pt–Pt distances will change as we move from the bulk to the surface and from terraces to steps and this will also effect overlap and bonding. Sattler[42] has commented that surface tension leads to reduced interatomic distances and discrete energy levels (rather than bands) at the surface. Antibonding interaction between the edge atoms (as well as between surface and bulk atoms) therefore produces greater reactivity as lobes are pushed out still further. Certainly the stepped surfaces are very active for

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[43] D. J. M. Fassaert, H. Verbeek, and A. van der Avoird, *Sur. Sci.*, 1972, **29**, 501.

[44] A. B. Anderson and R. Hoffmann, *J. Chem. Phys.*, 1974, **61**, 4545.

C–C, C–H and H–H bond breakage[45] (where the authors specifically speculate about directions or orbital emergence) and O_2 dissociative chemisorption.[46] *Dangling bonds* at surfaces with strong emergence of *d* orbital density at the corners of the cubic cluster Cu_8 have also been considered.[47] Common to the philosophy of all of the above authors is the presence of *unsaturated dangling bonds at the Pt surface*, which through *metal–ligand antibonding* interactions with near-neighbour atoms are raised to the energy of HOMO-E_f values; the atomic orbitals of each surface-Pt atom are directed even more out into the vacuum as a result of this antibonding interaction. They are thus even more able to react with adsorbates provided symmetry is conserved in such overlap.

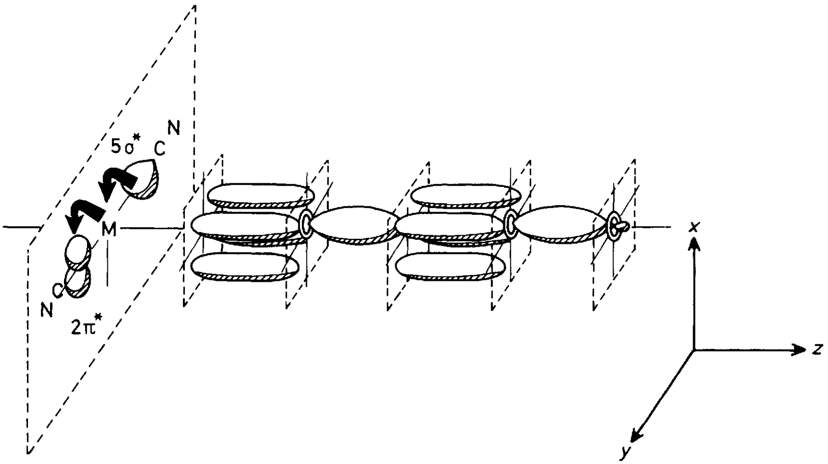

Figure 3 *Conjugated bonding in one-dimensional conductors containing* d^8Rh^+ *or* Pt^{2+} *in columns with weak* $\sigma_{d_{z^2}-d_{z^2}}$ *and* $\delta_{d_{xy}-d_{xy}}$ *metal–metal bonding. Resonance exists along the chain between equivalent descriptions of such bonding. The metal atoms sit at centres of square-planar coordination to* CN *groups bonded* via *metal*$_{d_{xy}}$–$CN_{2\pi^*}$ and metal$_{d_{x^2-y^2}}$–$CN_{5\sigma^*}$ *interactions as shown*

It is one aspect of the present consideration that this *simple concept that* d-*orbitals protrude from the surface and overlap with reactant MOs should perhaps be modified to consider paired-resonating metal orbitals.* Some years ago Ge and Si surfaces were thought[48] to have individual uncoordinated dangling bonds perpendicular to the surface; now it is judged these are few and far between and

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[45] R. J. Gale, M. Salmeron, and G. A. Somorjai, *Phys. Rev. Lett.*, 1977, **38**, 1027; G. A. Somorjai, *Adv. Catal.*, 1977, **26**, 1; G. A. Somorjai, *Catal. Rev.*, 1978, **18**, 173.

[46] D. M. Collins and W. E. Spicer, *Sur. Sci.*, 1977, **69**, 85.

[47] M. C. Desjonqueres and F. Cyrot-Lackmann, *Solid. State. Commun.*, 1976, **18**, 1127; J. R. Schrieffer and P. Soven, *Physics Today*, April 1975, **28**, 24.

[48] D. Tabor. *Proc. 2nd Eur. Conf. on Sur. Sci.*, 1979, North Holland, p. 6.

that they prefer to couple and share spins. Here then we consider whether this should not also be true for two-dimensional zero-valent group VIII or IB metal surfaces. Although Dowden[49] thought that the symmetry of the orbitals projecting from the surface suggested the type of bond which may form (σ, π, δ, *etc.*), most surface scientists have taken a more traditional view and considered the individual *d* orbitals emerge from the (100), (110), and (111) surfaces of a fcc metal,[50] suggesting that t_{2g} orbitals are delocalized but that e_g orbitals are localized (see left-hand side of Figure 4). However, later this localized surface model was amended[51] to indicate that while it was a valid description of a fcc metal surface substantially covered by adsorbed atoms, *for a bare metal surface there might be overlap between projecting orbitals causing a skin effect. Therefore we might take the view that in the absence of adsorbed species some overlap of surface orbitals of metals will undoubtedly occur and be responsible for surface properties; subsequent adsorption will lead to a relaxation of this overlap.* Blyholder considered[52] that adsorption on a metal atom in a surface would be affected by surrounding surface metal ligand-atoms; here consideration is given to the possibility that $\text{metal}_{\text{ligand}}$–$\text{metal}_{\text{central atom}}$ bonding in the surface involves multiple bonds (*e.g.* σ, π, *and* δ).

Table 1 indicates the atomic orbitals traditionally thought to exist at the surfaces of some crystallographic planes of a face-centred cubic group VIII or IB metal; also shown in Figure 4 are the equivalent σ, π, and δ orbitals which might exist thereon, assuming there is no significant hybridization as a result of differences in energies of *s*, *p*, and *d* atomic states of the metal. Whether atomic or molecular surface orbital states predominate obviously depends on the precise crystallographic plane (and presumably on the crystallographic habit of the metal too). However, what remains invariant for all such clean zero-valent metal surfaces is that (i) the $\sigma_{d_{z^2}-d_{z^2}}$ and $\sigma^*_{d_{z^2}-d_{z^2}}$ orbitals replace the atomic d_{z^2} states and (ii) the $\sigma^*_{d_{z^2}-d_{z^2}}$ antibonding molecular orbital state which protrudes from the surface is larger than the atomic d_{z^2} state and hence may be more accessible to adsorbates. The above simplified description ignores distortions arising from the surface changing the orbital point group symmetry, energy, and degeneracy (and hybridization). It has been applied to terrace surface atoms (*i.e.* those only deficient in *one* ligand adsorbate). *Atoms*

Table 1 *Angular emergence of* d *atomic orbitals at different faces of a fcc crystal*

	(100) *plane*			(111) *plane*	
molecular orbitals	*atomic orbitals*	*angle* (°)	*angle* (°)	*atomic orbitals*	*molecular orbitals*
π, π^*	d_{xy}	0.0	30.00	d_{xy}	σ, σ^*
δ, δ^*	d_{xz}	45.00	30.00	d_{xz}	δ, δ^*
π, π^*	d_{yz}	45.00	30.00	d_{yz}	π, π^*
σ, σ^*	$d_{x^2-y^2}$	0.00	36.27	$d_{x^2-y^2}$	σ, σ^*
σ, σ^*	d_{z^2}	90.00	36.27	d_{z^2}	σ, σ^*

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[49] D. A. Dowden, *Discuss. Faraday Soc.*, 1966, **41**, 256.

[50] G. C. Bond, *Discuss. Faraday Soc.*, 1966, **41**, 200; G. C. Bond, *Discuss. Faraday Soc.*, 1966, **41**, 211.

[51] G. C. Bond, *Sur. Sci.*, 1969, **18**, 24.

[52] G. Blyholder, *J. Phys. Chem.*, 1964, **68**, 2772.

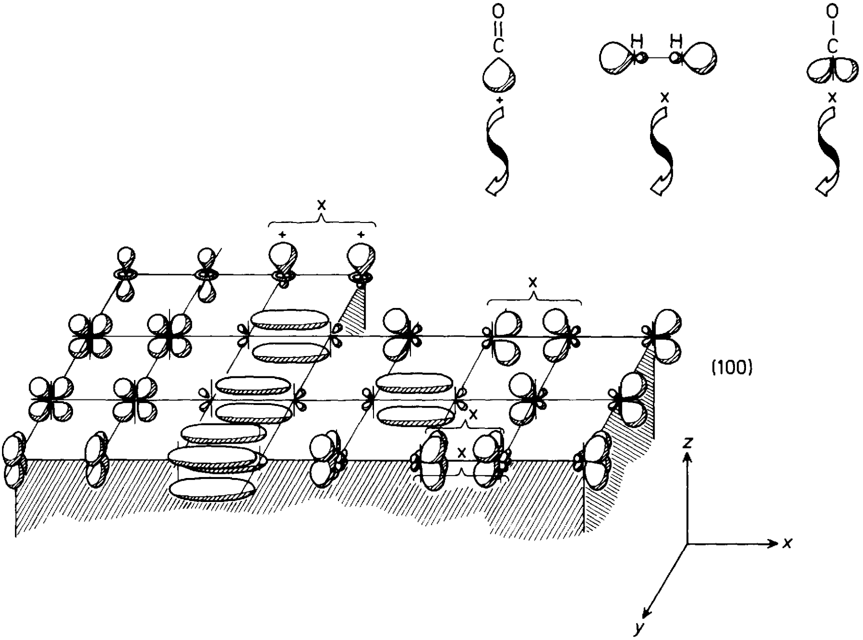

Figure 4 *Conjugated bonding at a two-dimensional metallic surface with* (100) (a) *and* (111) (b) *configuration developed from surface atomic orbitals shown at the left-hand side* (i.e. σ^*, π, π^*, σ, *and* δ^*). *First, these orbitals will be formed in a fluctuating manner from atomic orbitals and will 'wander' randomly about the surface to various resonant surface states. Second, two adjacent* (i) σ^*, (ii) π^*, and (iii) δ^* *can donate electrons to the* σ^* *state of* CO, *while the* $5\sigma^*$ *of* CO *can donate electrons to the* σ^* *metal orbital. Third, the* σ^*, δ^*, *and* π^* *surface orbitals are especially enlarged, accessible and reactive at edges and corners of the metal surface*

found at edges and corners also have enlarged π^* *and* δ^* *lobes protruding out of the lattice.* This may relate to the high reactivity of such low coordination sites, which was predicted[53] and is now accepted[54,55] for metal-catalysed C–C, C–H, and H–H bond breakage.

Clearly then, in both coordination chemistry *and* metal surfaces,[18,56] multiple bonds and antibonding molecular orbitals may critically affect reactivity.

Paired surface orbitals will be between adjacent metal–metal atoms with inevitable opportunities for various resonance states (see Figure 4). This will facilitate surface diffusion of adsorbates; we will return to this later. Although,

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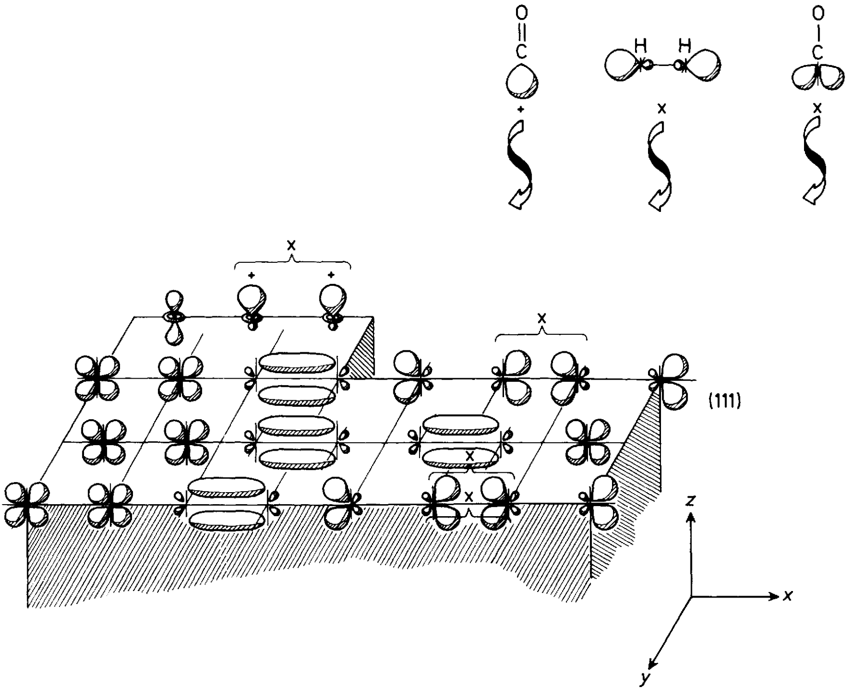
[53] H. S. Taylor, *Proc. R. Soc. London Ser. A*, 1925, **108**, 105.

[54] S. Siegal, J. Outlaw, and N. Garti, *J. Catal.*, 1978, **52**, 102.

[55] M. Salmeron, R. J. Gale, and G. A. Somorjai, *J. Chem. Phys.*, 1977, **67**, 5324; D. W. Blakely and G. A. Somorjai, *J. Catal.*, 1976, **42**, 181.

[56] R. Ugo, *Catal. Rev. Sci. Eng.*, 1975, **11**, 225; H. F. Schaefer, *Acc. Chem. Res.*, 1977, **10**, 287.



clusters predominantly consist of 'surface' metal atoms[42] their symmetry may not be identical to that at a zero-valent metal surface; discrete molecular orbitals in clusters may also replace the formal bands in solids.[57] Mingos[57] suggests metal–metal bonds in clusters have a higher *d*-orbital character than metal–ligand bonds. This will certainly be true for the group VIII and IB metals in low oxidation states considered here specifically whose reactivity may be defined by partially filled σ^*, π^*, and δ^* states.

C. Three-dimensional Metal–Metal Bonding.—Just as it is suggested here that σ, π, and δ metal–metal bonds exist in two-dimensional surfaces with resonance between various states, so the same can be true over three dimensions. Binary and ternary icosahedral compounds and quasi-crystals[58] of metals and alloys have been studied.[59] Icosahedral point group symmetry is incompatible with crystallographic

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[57] D. M. P. Mingos, *Chem. Soc. Rev.*, 1986, **15**, 31.

[58] D. Schectman, D. Blech, D. Gratias, and J. W. Cahn, *Phys. Rev. Lett.*, 1984, **53**, 1951; P. Villars, J. C. Phillips, and H. S. Chen, *ibid.*, 1986, **57**, 3085; P. W. Stephens and A. I. Goldman, *ibid.*, 1986, **56**, 1168; O. Biham, D. Mukamel, and S. Shtrikman, *ibid.*, 1986, **56**, 2191; M. Eibschutz, H. S. Chen, and J. J. Hauser, *ibid.*, 1986, **56**, 169; A. J. Melmed and R. Klein, *ibid.*, 1986, **56**, 1478; D. M. Follstaedt and J. A. Knapp, *ibid.*, 1986, **56**, 1827; F. C. Frank, *Proc. R. Soc. London. Ser. A*, 1952, **215**, 43.

[59] M. V. Jaric and U. Mohanty, *Phys. Rev. Lett.*, 1987, **58**, 230; P. Bak, *Phys. Rev. Lett.*, 1986, **56**, 861; J. B. Sokoloff, *Phys. Rev. Lett.*, 1986, **57**, 2223.

space filling schemes,[60] but an icosahedral arrangement of 13 transition metal atoms has a lower total energy than a close-packed crystal array structure[61] and metal–metal π-bonding therein may be involved.[62] Certainly icosahedral arrangements are known for microcrystals on catalyst surfaces (*e.g.* in small gold or silver particles[63]). Such a structure is most stable for particles containing 13, 55, 147, 309, 561 . . . atoms;[64] as a result such small colloidal particles are termed quasi-solids[63] or pseudo-solutions[65] to which neither solid nor liquid concepts of matter really apply.

3 Metal Reactivity

Orchin and Jaffe[66] have considered the importance of antibonding orbitals in defining the properties and reactivity of organic and inorganic molecules and metal carbonyl complexes; they emphasize that these are defined in large part by occupancy of antibonding molecular orbitals. Consider then if this is also true for metals on the right-hand side of the transition metal series.

Metal surfaces are characterized as good electron donors, with the *antibonding orbitals* of the adsorbate appearing to make a significant contribution to the *chemisorption bond.*[67] Does the resonant orbital approach used above have advantages over localized atomic orbital models of metal reactivity (as illustrated in references 68 and 69)?

Consider two aspects of metallic reactivity: CO chemisorption and H_2 chemisorption, both of which are of importance and well-modelled[70] in terms of the involvement of the localized *d* orbitals or the delocalized *d*-band. However, it is necessary to remember both bond order and symmetry considerations in chemisorption.[71]

The *chemisorption of gaseous CO* on metals has been very extensively studied and reviewed;[72,52] it may be dissociative or non-dissociative and linearly or bridge

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[60] L. Pauling, *Nature*, 1985, **317**, 512; L. Pauling, *Phys. Rev. Lett.*, 1987, **58**, 365.

[61] M. E. Eberhart, K. H. Johnson, D. Alder, R. C. O'Handley, and M. E. McHenry, *J. Non-Cryst. Solids*, 1985, **75**, 97; M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, *J. Magn. Magn. Mater.*, 1986, **54–57**, 279.

[62] M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, *Phys. Rev. Lett.*, 1986, **56**, 81.

[63] S. Iijima and T. Ichihashi, *Phys. Rev. Lett.*, 1986, **56**, 616; J. Emsley and P. Edwards, *New. Sci.*, 9 April 1987; A. C. Curtis, P. P. Edwards, D. A. Jefferson, B. F. G. Johnson, A. I. Kirkland, and D. E. Logan, *Angew. Chem.*, 1987, **26**, 676.

[64] A. L. Mackay, *Acta Cryst.*, 1962, **15**, 916.

[65] J. Th. G. Overbeek in 'Colloidal Dispersions', ed. J. W. Goodwin, Special Publication No. 43, The Royal Society of Chemistry, London, 1982, p. 1.

[66] M. Orchin and H. H. Jaffe, 'The Importance of Antibonding Orbitals', Houghton Mifflin, Boston, 1967.

[67] E. Shustorovich, R. C. Baetzold, and E. L. Muetterties, *J. Phys. Chem.*, 1983, **87**, 1100.

[68] D. B. Kang and A. B. Anderson, *Sur. Sci.*, 1986, **165**, 221.

[69] S. P. Wach and W. A. Goddard, *Sur. Sci.*, 1978, **72**, 645; J. M. MacLaren, J. B. Pendry, D. D. Vvedensky, and R. W. Joyner, *ibid.*, 1985, **162**, 322; J. M. MacLaren, J. B. Pendry, and R. W. Joyner, *ibid.*, 1986, **178**, 856.

[70] J. Harris, S. Andersson, C. Holmberg, and P. Nordlander, *Phys. Scr.*, 1986, **T13**, 155; J. P. Muscat and D. M. Newns, *Prog. Sur. Sci.*, 1978, **9**, 1.

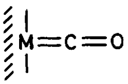
[71] R. C. Baetzold and E. M. Shustorovich, *Sur. Sci.*, 1986, **165**, L41; E. Shustorovich, *Sur. Sci.*, 1986, **176**, L863.

[72] G. Apai, P. S. Wehner, R. S. Williams, J. Stohr, and D. A. Shirley, *Phys. Rev. Lett.*, 1976, **37**, 1497; G. Broden, T. N. Rhodin, C. Brucker, R. Benbow, and Z. Hurych, *Sur. Sci.*, 1976, **59**, 593; S. Ishi, Y. Ohno, and B. Viswanathan, *Sur. Sci.*, 1985, **161**, 349; G. Doyen and G. Ertl, *Sur. Sci.*, 1974, **43**, 197; N. D. Spencer and G. A. Somorjai, *Rep. Prog. Phys.*, 1983, **46**, 1.

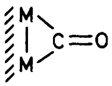
bound thereon. The adsorbate has electrons distributed in its molecular orbitals as $(1\sigma)^2\ (2\sigma^*)^2\ (3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma^*)^2\ (2\pi^*)^0$ and hence its $5\sigma^*$ and $2\pi^*$, which are predominantly on the C end of the adsorbate, are HOMO and LUMO levels. Blyholder[52] suggested two electron-transfers were involved in its chemisorptive bonding to metal M: (i) filled $\mathrm{CO}_{5\sigma}$*-to-unfilled $\mathrm{M}_{d_{z^2}}$ and (ii) back-donation[73] from the filled $\mathrm{M}_{d_{yz}}$-to-the unfilled $\mathrm{CO}_{2\pi^*}$. This synergistic bonding is analogous to complex carbonyl formation. However, recently, the role of the $2\pi^*$ CO orbital in preference to the $5\sigma^*$ orbital has been emphasized,[74] as has that of the 1π CO orbital.[75] Previously the specific mode of adsorption of CO upon (100) and (110) surface of fcc metals has been considered[50,76] only in terms of localized surface *atomic d* orbitals.

However, at clean metal surfaces we do not necessarily have dangling surface d_{z^2} bonds (see Figure 4). In symmetry terms there is reason to suppose that the $\mathrm{CO}_{5\sigma^*}$ orbital should donate directly to the metal $\sigma^*_{d_{z^2}-d_{z^2}}$ surface orbital on (100) or (111) surfaces of a face-centred cubic metal with subsequent destabilization of the metal *d*-states. In this context it is intriguing to note that the density of states of a metal is reported to be destabilized through an antibonding interaction with $\mathrm{CO}_{5\sigma^*}$ electrons.[77] Equally, back-donation from the metal $\pi^*_{d_{yz}-d_{yz}}$ molecular orbital to the $2\pi^*$ of CO would be possible on (100) surfaces of face-centred cubic transition metals since these would be of the correct symmetry and *larger* than surface atomic d_{yz} orbitals (see Figure 4a).

The proximity of adjacent $\pi^*_{d_{yz}-d_{yz}}$ orbitals on the (100) and (111) surfaces would suggest a tendency towards the bridge-bond state for CO thereon at low CO coverage, while d_{xy} orbitals produced by adsorbate induced-metal isolation at high coverage might be involved in $d_{xy} \rightarrow \mathrm{CO}_{2\pi^*}$ linearly binding CO[78] at high coverage.



and



For group VIII–IB metals on the right of the transition elements $\pi^*_{d_{yz}-d_{yz}}$ and d_{yz} surface states will be largely filled, and non-dissociative chemisorption is dominant at room temperature. Clearly the energy of relevant surface paired orbitals of the metal and those of CO are also important in defining the degree of orbital overlap.

The ability of $\pi^*_{d_{yz}-d_{yz}}$ resonant metal–metal orbitals to flip between alternative positions as suggested by Pauling[15] and so to 'migrate' across the surface is a good

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[73] N. Crisa, G. Doyen, and F. V. Tentini, *Sur. Sci.*, 1985, **162**, 120.

[74] J. Rogozik and V. Dose, *Sur. Sci.*, 1986, **176**, L847.

[75] I. A. Howard, G. W. Pratt, K. H. Johnson, and G. Dresselhaus, *J. Chem. Phys.*, 1981, **74**, 3415.

[76] C. Wang and R. Gomer, *Sur. Sci.*, 1979, **90**, 10; P. W. Tamm and L. D. Schmidt, *J. Chem. Phys.*, 1969, **51**, 5352.

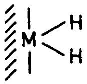
[77] F. Raatz and D. R. Salahub, *Sur. Sci.*, 1986, **176**, 219.

[78] J. T. Yates and C. W. Garland, *J. Phys. Chem.*, 1961, **65**, 617.

reason for surface diffusion[79] of CO, especially on the (100) crystallographic plane. This model therefore readily accounts for modes of CO chemisorption on a transition metal M[56] *and* its spillover[79] and surface diffusion.

CO chemisorption on the surfaces of group VIII–IB metals is normally largely non-dissociative. Nevertheless, on Pt(100) the CO may tilt 16° to the normal, and on Fe(100) this transformation is taken further with it being noted[80] that CO can lie parallel to the surface. This would be the precursor of CO decomposition; traditionally this parallel position is thought to arise from vibrational deformation, but with the present model one can see that one $(\pi^*_{d_{yz}-d_{yz}})\underset{\text{metal}}{\longrightarrow}(CO_{2\pi^*})$ interaction at the C end of the adsorbate could be complimented by a $(\pi^*_{d_{yz}-d_{yz}})\underset{\text{metal}}{\longleftarrow}(CO_{1\pi})$ interaction at the O end in such a diadsorbed state.

The *chemisorption of H atoms* on a metal surface has been considered,[81] and ion-beam mass spectrometry has been used by Elkind *et al.* specifically to probe the role of *d*-orbitals in the interaction of H_2 (D_2 and HD) with transition metal ions. For molecular dihydrogen adsorbing onto a metal surface it is possible that there is electron donation from metal atomic orbitals to the unfilled σ^* adsorbate molecular orbital. This would destabilize dihydrogen allowing dissociation to adsorbed hydrogen atoms.[82] However, it would be equally possible for the surface $\sigma^*_{d_{z^2}-d_{z^2}}$ existing here on the (100) and (111) surfaces if at least partially filled (as it would be on the right-hand side of the transition series where we already know group VIII metals are good hydrogenation catalysts) to donate to the σ^*H_2 molecular orbital (see Figure 4), but alternatively it would be even better for adjacent $\pi^*_{d_{yz}-d_{yz}}$ molecular orbitals to interact directly with the σ^* antibonding orbital of H_2 and, as a result, for the dihydrogen to dissociate directly (see Figure 4). This model again readily accounts for the possible modes[56] of chemisorption on a transition metal M



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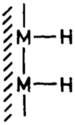

at least as well as any other.[83] If antibonding and bonding states can so interact during hydrogen chemisorption and this is symmetry forbidden, a high activation energy arises,[70] however the present analysis goes further and it is interesting that it suggests that a minimum number of metal atoms may be required for hydrogen chemisorption.[84] In addition surface spillover, diffusion, and H_2–D_2 exchange are

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[79] M. Tringides and R. Gomer, *Sur. Sci.*, 1986, **166**, 419; M. Tringides and R. Gomer, *Sur. Sci.*, 1986, **166**, 440.

[80] C. Benndorf, B. Kruger, and F. Thieme, *Sur. Sci.*, 1985, **163**, L675; M. I. Ban, M. A. van Hove, and G. A. Somorjai, *Surf. Sci.*, 1987, **185**, 355.

[81] D. Newns, *New Sci.*, 1977, 132; F. Flores, N. H. March, and C. J. Wright, *Phys. Lett.*, 1977, **64A**, 231; F. Flores, N. H. March, and I. D. Moore, *Sur. Sci.*, 1977, **69**, 133; J. L. Elkind and P. Armentrout, *J. Phys. Chem.*, 1987, **91**, 2037.

[82] K. H. Johnson, A. C. Balazs, and H. J. Kolari, *Sur. Sci.*, 1978, **72**, 733.

[83] R. C. Baetzold, *J. Catal.*, 1973, **29**, 129; A. van der Avoird, *Sur. Sci.*, 1969, **18**, 159.

[84] M. E. Geusic, M. D. Morse, and R. E. Smalley, J. Chem. Phys., 1985, **82**, 590.

explained with resonance[15] of surface $\pi^*_{d_{yz}-d_{yz}}$ orbitals amongst different alternative positions mixing and carrying the dissociated adsorbate with them. Furthermore, the proposed interactions in hydrogen chemisorption would be easiest at low coordination edge and corner sites where $\sigma^*_{d_{yz}-d_{yz}}$ and $\sigma^*_{d_{z^2}-d_{z^2}}$ orbitals show even greater enlargement and availability. Thus it comes as no surprise that such step sites increase the rate of H_2–D_2 exchange[45] and the sticking probability of H_2.[85] Previously[40] it has been suggested this is due to the greater availability there of protruding or dangling occupied d_{yx} orbitals at such low coordination sites. Here we consider that these may rather be d_{yz}–$d_{yz}\pi^*$ molecular orbitals, which protrude still more. Analysis of *paired* interacting orbitals has been applied to H_2 chemisorption on Ni.[86]

Therefore, consistent with earlier evidence, we conclude that metal atoms at edges are expected to have different electronic properties to those atoms in the bulk or low index planes[85] and this must affect hydrogen adsorption. Certainly Christmann *et al.*[87] believe that the energy with which hydrogen is adsorbed on structural imperfections on Pt(111) is higher than on the perfect surface terrace. Interestingly, though, Martensson *et al.*[88] consider the step sites should also have a substantial number of *d*-holes.

4 Discussion of Metallic Reactivity and Bonding

Previous suggestions[40,50,51] have been that d_{z^2}, d_{yz}, and d_{xz} orbital lobes will extend from the Pt surface and could therefore be involved in catalysis and chemisorption as 'dangling' bonds. However, here $\sigma^*_{d_{z^2}}$ and $\pi^*_{d_{yz}-d_{yz}}$ molecular orbitals, which are larger and of equal occupancy, are invoked; such metal–metal bonds are very weak and hence very reactive. One further point is that since the $\pi^*_{d_{yz}-d_{yz}}$ surface orbitals resonate amongst the various positions between adjacent atoms, this leads directly to surface hydrogen and CO diffusion. The resonance of partially filled molecular orbitals at a surface is analogous to Pauling's approach to the bonding in bulk metals. In the past there have been two extreme approaches to metallic bonding and reactivity: (i) collective and electron band;[89] (ii) localized – valence bond.[50,51,90] The generalized valence bond approach has been applied to bonding in metal clusters, but predominantly in terms of σ-bonding.[91]

The present analysis is a combination of these two, and involves both occupied and vacant[92] *d*-states and *especially antibonding* π* *and* σ* *states.* Analogies exist between metal–metal bonding and reactivity and that seen in clusters,[93]

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[85] K. Christmann and G. Ertl, *Sur. Sci.*, 1976, **60**, 365.

[86] H. Fujimoto and H. Kawamura, *J. Phys. Chem.*, 1987, **91**, 3555.

[87] K. Christmann, G. Ertl, and T. Pignet, *Sur. Sci.*, 1976, **54**, 365.

[88] A. S. Martensson, C. Nyberg, and S. Andersson, *Phys. Rev. Lett.*, 1986, **57**, 2045.

[89] F. O. Goodman, *Sur. Sci.*, 1987, **180**, 460, 477.

[90] H. J. Brocksch and K. H. Bennemann, *Sur. Sci.*, 1985, **161**, 321 or 821; J. B. Goodenough, 'Magnetism and the Chemical Bond', Interscience, 1963.

[91] M. H. McAdon and W. A. Goddard, *Phys. Rev. Lett.*, 1985, **55**, 2563; *J. Non-Cryst. Solids*, 1985, **75**, 149; *J. Phys. Chem.*, 1987, **91**, 2607.

[92] O. Johnson, *J. Catal.*, 1973, **28**, 503.

[93] 'Metal Clusters in Catalysis', 'Studies in Surface Science and Catalysis', ed. B. C. Gates, L. Guczi, and H. Knozinger, Elsevier, Amsterdam, 1986.

complexes,[54] and the organic solid state. If electrons are lost from molecular antibonding σ^* or π^* or δ^* orbitals at the metal surface by electron donation to the antibonding states of the adsorbate then we can see that metals themselves *benefit* from the stabilization induced by chemisorption and are not acting as impartial benefactors. Indeed the dimension of delocalization perpendicular to the adsorbing surface L_i could be increased by adsorption with increased stabilization to the metal adsorbent. The symmetry of metal and adsorbate orbitals is clearly critical and it may be that the equivalent of frontier-orbital analysis[94] is applicable. Although a relationship may exist between organo-metallic chemistry and surface chemistry,[95] metal–metal bonds at Pd(111) surfaces retain much of their d^{10} character and this may mean that bare Pd clusters are poorer models of Pd surfaces, *i.e.* the relationship is weaker than earlier supposed.

With a better understanding of this bonding it ought to be possible to prepare catalysts with a high density of specific sites for definite functions in catalysis. For example, if adjacent metal atoms are translated or rotated relative to one another[23] π and δ bonding can be created or removed.

It has become clear that the structure of metals (and alloys) can be represented in terms of covalent bonds that resonate among alternative interatomic positions; metal-ligate resonance, in one-, two-, and three-dimensional metals *is possibly more important for such metallic systems than in more familiar aromatic and conjugated hydrocarbon molecules.* Characteristic features of metals are determined by this unsynchronized resonance of individual valence bonds. Such resonating orbitals may be equivalent to those termed metallic orbitals;[15] they form a delocalized state or *orbital reaction 'skin' above the metal surface.*

Molecular orbital theories are notoriously difficult to apply fully to clusters, metals, chemisorption, and catalysis;[96] extreme models of the solid state can be bulk or atomic but here we have an alternative description of metal bonding and reactivity for group VIII and IB metals using resonating orbitals which combine features of both localized and delocalized states. Although this does not invoke hybridization for group VIII–IB metals, it is appreciated that hybrid *d–s–p* orbitals are very important for earlier transition metals;[97] despite *d–s–p*-hybridization assumed[90] in Pt(110) with metal–metal bonds 50 pm shorter than equivalent single metal bonds.[98] This itself suggests elements of multiple Pt–Pt bonds of the form proposed here. Thankfully, *d* (and *p*) orbitals will largely define the general spatial geometry of the hybrid orbitals; in view of the energies of atomic states for the zero- or low-valent group VIII and IB metals the present approach is qualitatively useful in the context of their bonding and reactivity here considered. Since the *d* atomic states of group VIII–IB metals are largely filled, their overlap produces almost equal numbers of filled bonding and antibonding molecular orbital states which do not contribute greatly to bulk *bonding*. Nevertheless, the

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very weakness of this bonding makes it *ideal* in terms of contributions to *reactivity*. Chemisorption is a *local* process involving only a few nearest adsorbent atom neighbours with the adsorbate[95] and the present *paired-local* surface orbitals are thus especially relevant; such local interactions are thus best described by the local orbital characteristics.[99]

Further work will be needed with respect to the properties of other metals; certainly the σ^* and δ^* orbitals prevailing at other fcc metal surface planes or at surface planes of bcc or cph VIII–IB metals will be different, and yet the philosophy developed here will be equally applicable at each particular surface. More attention to hybrid sp^3d^2, sd^3, or p^3d^3 states[97] will need to be given for metals to the left in the transition metals; where again partially occupied bonding (rather than antibonding) M–M states will also be more important than here. Trends in chemisorption, catalysis, and reactivity of transition metals with periodic position require further work therefrom. In addition, so far we have only considered homonuclear metal–metal bonding. Both bimetallic clusters and alloys are increasingly important in catalysis. However, the differences in metal electronegativities are so small between adjacent period columns that the effect of the present resonant orbital structures would be small in Pt–Au, but would be much larger in Pt–Sn wherein π^* and σ^* molecular orbitals would be predominantly on the Pt. This is an intriguing interpretation of promotion of Pt in real heterogenous catalysts in terms of non-symmetrical multiple bonds at the bimetallic surfaces. In this context it is interesting to note that Sn additions to Pt weaken $5\sigma^*$CO bonding to Pt.[100]

5 Conclusions

Metal clusters[42,57,101] are midway between complexes and bulk metal crystallites.[102] As atoms are added to the cluster it moves towards a system of relevance to heterogeneous catalysis, and as atoms are removed it becomes closer to homogeneous catalysis. When the clusters contain 50 metal atoms they must be approaching the size of metal crystallites; thus we may have band structures and local orbital descriptions of both metal clusters and crystallites.[57] With time there has been steady progress towards smaller metal crystallites and larger clusters, whose properties may become coincident or tangential.[103] Resonant metal–metal bonding in one-, two-, and three-dimensions provides a useful description of the bonding and reactivity of metals, despite uncertainties in the faces exhibited at microcrystal metallic surfaces[104] and if these

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are changed by adsorption,[105] reconstruction,[106] and catalytic properties.[107]

Since even the surface of metastable insulator diamond with its three-dimensional sp^3 bonding has been found to have dimerized chains of π-bonds (formed by p_z–p_z overlap or sp^3–sp^3 overlap) when clean, and these only revert to dangling =C–H bonds when hydrogenated, the multiple bonds envisaged here are both likely and important for metals in one-, two- and three-dimensional solid states, and possibly for all but the most ionic surfaces of transition metal compounds.[108] If the metal–metal bonding here can be probed and subsequently controlled then 'we cannot doubt but that the final solution of the problem of the metallic state will mark a new epoch . . .'[109] in the development of catalysts, solid state conductors, and fuel cell electrodes. Thus a constraining oxide support may affect metal orbital states. In the light of the above predictions of the different reactivities based on a resonant bonding model it may not be surprising that different types of site can appear on specific types of metal crystallite,[110] whose size will so affect[111] the dimensions of delocalization in any direction L_i and hence the local E_f.

However, progress will require the availability of suitable analytical tools. The surface geometry of metals can be probed (in reciprocal state by LEED[112] and by high resolution electron microscopy[113]) and so can the spatial geometry of filled and unfilled surface electron states using angle-resolved photoelectron spectroscopies[114] and inverse photoemission.[115] For example, in the later context, elegant photoemission results[116] have shown that for body-centred tungsten the e_g d orbitals emerge at 90°, 45°, and 90° to the (001), (111), and (010) planes. Nevertheless, such methods would not differentiate $\pi^*_{d_{yz}-d_{yz}}$ orbitals at a metal (100) surface from the atomic d_{yz} states. However, the new technique of scanning tunnelling microscopy (STM) appears promising. STM has now been applied to the study of a wide range of solid surfaces,[117] especially semiconductors,[118]

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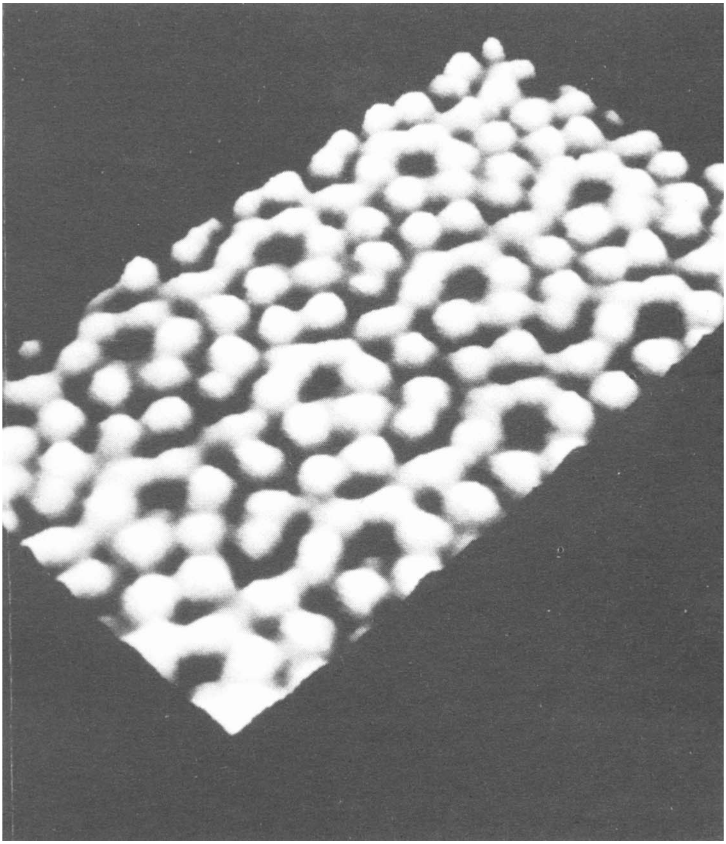

Figure 5 *Scanning tunnelling microscopy of pairing of* Si *surface states on a* (111) *surface*[121]

metals,[119] and graphite[120] where it reveals the perfection of the surface geometry at an atomic level. From the particularly fine computer-enhanced STM image in Figure 5 of an Si(111) surface[121] it appears STM can reveal surface orbital directions and surface bonding. The evidence of orbital coupling at the surface of Si revealed by STM in Figure 5 is particularly relevant to the thrust of the present paper in the light of Tabor's comments[48] on the coupling of dangling bonds at Si surfaces when these were in a vacuum. Maybe now STM will be applied to the

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metallic state in one-, two-, and three-dimensions; it has the advantage of being usable in UHV *and* high pressure and is thus capable of looking at clean and adsorbate-covered surfaces[122] and catalysts.

Group VIII–IB metal bonding and reactivity is crucial in heterogeneous catalysis, selective adsorption, corrosion, and electrocatalysis; it is certainly true that chemical bonds outside the metal surfaces involving antibonding molecular orbitals are pivotal.[123]

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