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Unified LCAO MO Approach to Chemisorption and Heterogeneous Catalysis. 2. The Cluster–Solid Analogy and Surface vs. Bulk Charge Distribution

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Abstract: Some general aspects of the cluster–solid analogy are discussed. Surface vs. bulk charge distributions have been considered for various metals within the framework of a simple Hückel-type LCAO MO analytical model. It has been shown that for the s^1 occupation in homonuclear metal clusters $M_{n+1} = MM'_n$, with n equivalent ligands M′, the central atom M will be positive and the outer atoms M′ are negative ("the s^1 hypothesis"). This result has been extended for the general $s^Sp^Pd^D$ occupancy in both clusters and solids. The surface vs. bulk orbital occupancy is determined by the metal effective occupation number. For alkali, noble, and group 6–8 transition metals, the surface atoms will have the larger $S + D$ value, but for transition metals of group 4 and probably group 5 the interior atom sd orbitals may be more occupied. The above conclusions have been verified by the extended Hückel and CNDO calculations on the relevant model (cluster) compounds. Some implications of the results obtained are discussed and compared with those of other authors, showing encouraging agreement with published theoretical and experimental data. Serious limitations of the effective-charge concept are stressed.

Introduction

In an attempt to simulate solids by metal clusters, the cluster–solid analogy has been developed extensively (see main references in our first paper[1]). This analogy, however, is not well defined because there are no clear criteria showing how to proceed from finite clusters to infinite solids. Any cluster consisting of 10–100 atoms, which can be treated computationally by the existing MO methods, "would be sorely inadequate for the discussion of a number of solid state aspects... Such aspects as accurate, values of bulk cohesive energies, work functions and any effects associated with the Fermi surface are clearly outside the scope of these clusters."[2] Also, for many physical and computational reasons, the first-principles methods appropriate for atoms and molecules (first of all, the Hartree–Fock (HF) method) usually are not suitable for band computations.[3] Because there is no computationally satisfactory way to correlate the electronic structure of molecules (clusters) and solids, it makes sense to try various independent electron models (which are qualitatively applicable to all systems from diatomic molecules to solids) and verify them by the proper model calculations.

This paper considers, in this way, some aspects of the cluster–solid analogy concerning the surface-bulk charge distribution and orbital rehybridization. Geometric nonequivalence of surface vs. bulk metal atoms should result in some nonuniform distribution of the electron density, which can be expressed in terms of nonequal effective charges of these atoms and rehybridization of their valence orbitals (s, p, d). These changes may be of crucial importance for understanding differences in the properties of various surfaces (their work functions, chemisorption, catalytic activities, etc.). We will attack the above problems first within some simple Hückel-type LCAO MO analytical models and then verify the model predictions by the extended Hückel (EH) and CNDO calculations on the relevant (model) clusters. Finally, we will compare our results with those of other authors.

Results and Discussion

(1) Analytical Model Results. The s Charge Distribution. Consider first the cluster MOs formed by metal s orbitals. Let us begin with some homonuclear metal cluster M_{n+1}, or MM'_n, where the central atom M is coordinated to n geometrically equivalent ligands M′; M′ is chemically identical with M. For interatomic distances, we have $R(M-M') \leq R(M'-M')$ where the sign "equal" corresponds to the extreme case of close packing. The simplest examples are MM'_2 $D_{\infty h}$, MM'_3 D_{3h}, or MM'_6 O_h. In the context of the cluster–solid analogy, the most interesting clusters are cubic (O_h), bcc M_9 (MM'_8), and fcc M_{13} (MM'_{12}). In all these cases there is one and only one totally symmetric group ligand orbital

$$[s]_n = \frac{1}{\sqrt{n}}(s_1 + s_2 + \ldots + s_n) \qquad (1)$$

which belongs to the A_1 representation and interacts with the central atom orbital, s_c, giving the doubly occupied bonding MO ψ_1 (eq 2) of the form

$$\psi_1 = as_c + b[s]_n \qquad (2)$$

and its antibonding counterpart

$$\psi_1^* = bs_c - a[s]_n \qquad (3)$$

where

$$a > 0,\ b > 0,\ a^2 + b^2 = 1 \qquad (4)$$

As earlier,[4-7] we neglect overlap integrals $S_{ij} = \langle s_1|s_j\rangle$, $i \neq j$, in the normalization coefficients but do not neglect resonance integrals $H_{ij} = \langle s_i|H|s_j\rangle$, $i \neq j$, which determine the differences in energies of various group ligand orbitals. Because only the MOs in eq 2 and 3, by definition, include s_c, all other MOs will embrace the outer atoms only.

Electroneutrality of clusters corresponds to a singly occupied s orbital per atom, the s^1 model. We can formulate the following general statement: within the s^1 model, in metal clusters MM'_n with all outer atoms M′ equivalent, $R(M-M') \leq R(M'-M')$, the central atom is positive so that the outer atoms are negative. In other words, the central–outer atom charge distribution is

$$q_c > 0,\ q' < 0 \qquad (5)$$

or, in terms of relative charges,

$$\delta_M{}^+ - \delta_{M'}{}^- \qquad (5')$$

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[1] Part 1: Shustorovich, E.; Baetzold, R. C., submitted for publication to *Inorg. Chem.*

[2] Messmer, R. P. In "The Nature of the Surface Chemical Bond", Rhodin, T. N., Ertl, G., Eds.; North-Holland Publishing Co.: Amsterdam, 1979; p 60.

[3] See, for instance, (a) Dimmock, J. O. *Solid State Phys.* **1971**, *26*, 104–274. (b) Monkhorst, H. J. *Phys. Rev. B* **1979**, *20*, 1504, and references cited therein.

[4] Shustorovich, E. *Inorg. Chem.* **1978**, *17*, 2648.

[5] Shustorovich, E. *J. Am. Chem. Soc.* **1978**, *100*, 7513.

[6] (a) Shustorovich, E. *J. Am. Chem. Soc.* **1979**, *100*, 792. (b) *Inorg. Chem.* **1979**, *18*, 1030.

[7] Shustorovich, E.; Dobosh, P. A. *J. Am. Chem. Soc.* **1979**, *101*, 4090.

[8] The only exception to this trend is fcc M_{19} (see Table I), but here the relation between the second layer (M'_{12}) and surface (M''_6) atoms is especially ill defined.

[9] (a) Melius, C. F.; Upton, T. H.; Goddard, W. A. *Solid State Commun.* **1978**, *28*, 501. (b) Melius, C. F. *Chem. Phys. Lett* **1976**, *39*, 287.

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Table I. Calculated Charge Distributions Using s^1 Model for Some Silver Clusters

cluster	method	$R_{MM'}$, Å	effective charges[a]					
			q_c	q'_2	q'_3	q'_4	q'_5	q'_6
Ag_{13}	CNDO	3.4	+0.54	−0.05				
Ag_{13}	EH	2.5	+0.55	−0.05				
Ag_{19}	EH	2.5	+0.27	−0.05	+0.06			
Ag_{43}	EH	2.5	+0.16	+0.07	+0.14	−0.08		
Ag_{55}	EH	2.5	−0.03	+0.27	−0.13	−0.03	−0.15	
Ag_{79}	EH	2.5	+0.41	+0.05	+0.15	+0.12	−0.04	−0.18

[a] q'_i indicates the average charge within the *i*th shell as measured from the fcc cluster center (see also footnote *a*, Table II).

This statement, which for brevity we will refer to as "the s^1 hypothesis", seems to be strict, at least within the Hückel-type formalism. The proof includes an explicit analysis of all the relevant clusters MM'_n, from MM'_2 $D_{\infty h}$ up to MM'_{12} O_h.[10a] The general idea is as follows. Because $[s]_n$ (eq 1) is totally symmetric, its energy will be *lowest* among all other symmetry-adapted ligand orbitals and, in particular, it will always be lower than that of s_c. Therefore, in eq 2

$$a < b \tag{6}$$

so that from eq 4 we have

$$a^2 < \frac{1}{2} \tag{7}$$

and in the case of the vacant ψ_1^* (eq 3)

$$q_c = 1 - 2a^2 > 0,\ q' = -(q_c/n) < 0 \tag{5''}$$

Only this case is possible because ψ_1^* (eq 3) will be the highest or next to the highest MO[10a] (the latter is just a case in fcc M_{13}; see Figure 1a). Moreover, if ψ_1^* (eq 3) were occupied, we would have $q_c < 0$ ($-a^2$ or -1 for singly or doubly occupied ψ_1^*, respectively) and $q' > 0$. In this case, however, the relative energy of s_c would be even higher so that none of the charge iteration procedures can be self-consistent.[10a,18] For this reason we believe that "the s^1 hypothesis" should be valid within the HF formalism as well.

Consider further a cluster $MM'_{n_1}M''_{n_2}$ where there are two sets of equivalent ligands, M′ and M″. In such a case, within the A_1 representation we have two relevant symmetric group ligand orbitals, one for each group of equivalent ligands, namely

$$\begin{aligned} [s]_{n_1} &= \frac{1}{\sqrt{n_1}}(s_1 + s_2 + \ldots + s_n) \\ [s]_{n_2} &= \frac{1}{\sqrt{n_2}}(s_{n_1+1} + s_{n_1+2} + \ldots + s_{n_1+n_2}) \\ n_1 + n_2 &= n \end{aligned} \tag{8}$$

Thus, we will have three A_1 MOs including s_c where two of them, $1a_1$ and $2a_1$, are occupied (doubly and singly, respectively[19]). On the basis of fundamental properties of three-orbital interactions,[4,5,7] one can show[10a] that in M_{19} vs. M_{13} the electron densities on the center (first shell) atom M should be increased so that q_c will be less positive (see Tables I and II).

In the further fcc spherical clusters $MM'_{n_1}M''_{n_2}$... (with complete successive shells), M_{43}, M_{55}, M_{79}, etc., the A_1 representation will contain as many group ligand orbitals as the number of shells (for instance, two, eq 8, in $MM'_{12}M''_6$). Thus, the effective charge on the center atom will be further decreased and can become negative and again positive depending on its involvement in the relevant A_1 MOs (see Tables I and II). For other atoms the results are not obvious because the self-consistent charge iteration may result in nonmonotonic trends for atomic charges in different shells. However, we are interested in the charge distribution within the infinite solids rather than the finite, specific clusters. For this reason we consider some very big metal cluster $M(M')_{n_1}(M'')_{n_2}(M''')_{n_3}$... where M′ plays a role of the central atom with respect to M″, etc. Because of $q' < 0$ (eq 5), the inequality in eq 6 can only be strengthened when the new central atom M′ will be surrounded by a new set of neutral metal ligands M″. Thus, the basic inequality $q_c > q'$ in M_{13} (eq 5) can be replaced for $q_{\text{second layer}} > q_{\text{surface}}$ in bulk metals which, in terms of relative charges, should correspond to $\delta_{\text{sec}}^+ - \delta_{\text{surf}}^-$. In other words, in the framework of the "s^1 model" the surface atoms will be more negative as compared with the bulk atoms.[8]

So far we have considered the s^1 case. It is clear, however, that the interrelations of q vs. q' will depend on the s occupancy, s^x. Indeed, the effective charge on the ligand atoms, $q' = q_j'$ ($j = 1, 2, \ldots, n$) will be

$$q' = 1 - \frac{2b^2}{n} - \sum_i^{\text{occ}} r_{ij}q_{ij} \tag{9}$$

where we sum over all the occupied nonsymmetric MOs, ψ_i, $i = 2, 3, \ldots$; r_{ij} is the occupation number. In the electroneutral case, $x = 1$, we obviously have $q' = -(q_c/n) < 0$ (eq 5″). In the model anionic case we can increase x such that

$$1 \le x \le 2 \tag{10}$$

so that q_c or the difference $q_c - q' = q_c(n + 1)/n$ will only be increased due to occupation of a larger number of the nonbonding MOs, which decreases q' (eq 9) via the terms $\sum_i^{\text{occ}} r_{ij}q_{ij}$. On the contrary, in the model cationic case we can decrease x such that

$$0 \le x < 1 \tag{11}$$

so that a smaller number of the nonbonding MOs will be occupied and q' (eq 9) will be increased via the terms $\sum_i^{\text{occ}} r_{ij}q_{ij}$, so that we can expect some critical value of $x = x_{\text{cross}}$ for which a crossover of the q_c and q' curves ($q_c = q' = 0$) must take place.

The "s^1 model" can in principle be applied not only to group 1 metals (alkali, 1A, and noble, 1B) but also to some transition metals where the electron configuration d^{N-1}s^1 has been suggested.[3,9] In the general case, however, one should consider the "s^x model" modified by the possible p and d contributions.

The p and d Charge Distributions. The relevant symmetry-adapted linear combinations of the p and d orbitals will be more complicated than those of the s ones (eq 1–7). Nevertheless, they can be analyzed along the same lines[10a] and the main results are rather obvious. Again, in fcc M_{13}, for each $\psi = p_x, \ldots d_{z^2}, \ldots d_{xz}, \ldots$ within the relevant irreducible representation Q_i(t_{1u}, e_g, t_{2g}) we have the doubly occupied MO ψ_1 (eq 2′) of the form

$$\psi_1(\phi) = m\phi_c + n[\phi]_{Q_i} \tag{2'}$$

and its antibonding counterpart

$$\psi_1^*(\phi) = n\phi_c - m[\phi]_{Q_i} \tag{3'}$$

$$m > 0,\ n > 0,\ m^2 + n^2 = 1 \tag{4'}$$

The charge separation, $q_c - q'$, should be determined as a function of the occupancies, p^x and d^x. Remember that in terms of electronic configurations, the s^1 case will approximately correspond to the p^3 and d^5 cases, respectively.[11]

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(10) (a) Shustorovich, E., unpublished results (available upon request). (b) Part 3: to be submitted to *J. Am. Chem. Soc.*

(11) In cubic (O_h) clusters (lattices) the p level (band) is triply degenerate but the d level (band) is split into two sublevels (subbands), e_g (d_{z^2}, $d_{x^2-y^2}$) and t_{2g} (d_{xz}, d_{yz}, d_{xy}). This splitting is not important, however, for the ensuing consideration.

(12) More strictly, for the metal electron population s^{S}p^{P}d^D the sum $N = S + P + D$ is constant but all the components are, in principle, some functions of geometry, size, and the nature of M itself. Because P should be rather small, $N \simeq S + D$ and typically the redistribution of the s and d densities is size dependent. In particular, for ending transition metals, as the cluster size increases the s occupation decreases and the d one increases, resulting in s^{x}d^{N-x}, $x \ll 1$, for the bulk metals; cf. the size-dependent X-ray photoemission and absorption spectra of the Pd and Pt clusters (on carbon substrates)[13] and the magnetic[14] and de Haas-van Alphen[15] measurements on bulk metals. This s-d density redistribution, however, may be important for the bulk-surface charge distribution (see text).

(13) (a) Mason, M. G.; Gerenser, L. J.; Lee, S.-T. *Phys. Rev. Lett.* **1977**, *39*, 288. (b) For the Pd clusters (on carbon) the L-edge area of the X-ray absorption, PdL_{III} (2p → 4d), distinctly shows an increase of the d occupancy as the cluster size increases (Apai, G., unpublished results).

Table II. Calculated EH Charge Distributions for M_{13} Clusters

			center atom				outer atom			
cluster	basis	$R_{MM'}$, Å[a]	q_c	s	p	d	q'	s	p	d
Cu_{13}	s,p,d	3.0	+0.41	0.48	0.17	9.94	−0.03	0.91	0.15	9.97
		2.5	+0.52	0.47	0.12	9.89	−0.05	0.86	0.23	9.96
Ag_{13}	s,p	3.0	+0.38	0.48	0.15		−0.03	0.97	0.06	
		2.5	+0.40	0.46	0.13		−0.03	0.91	0.12	
Ag_{13}	s,p,d	3.0	+0.39	0.49	0.17	9.95	−0.03	0.98	0.08	9.97
		2.5	+0.45	0.51	0.20	9.83	−0.04	0.93	0.19	9.92
Ni_{13}	s,p,d	3.0	−0.33	0.51	0.07	9.75	+0.03	0.33	0.02	9.62
		2.5	−0.17	0.49	0.06	9.62	+0.01	0.44	0.05	9.50
Pd_{13}[b]	s,p,d	3.0	−0.30	0.57	−0.18	9.92	+0.03	0.30	−0.03	9.71
		2.5	−0.08	0.51	−0.37	9.93	+0.01	0.43	−0.07	9.63
Pt_{13}	s,p,d	3.0	+2.84	0.53	0.52	6.11	−0.24	0.74	0.26	9.24
		2.5	+3.25	0.42	0.38	5.95	−0.27	0.73	0.50	9.04
Rh_{13}	s,p,d	3.0	+2.88	0.54	0.18	5.36	−0.23	0.29	0.06	8.88
		2.5	+2.93	0.54	0.35	5.17	−0.24	0.45	0.15	8.64
Ru_{13}	s,p,d	3.0	+1.76	0.61	0.39	5.24	−0.15	0.63	0.09	7.43
		2.5	+1.89	0.59	0.48	5.04	−0.16	0.67	0.21	7.28
Mn_{13}	s,p,d	3.0	+1.12	0.53	0.12	5.23	−0.09	0.27	0.03	6.79
		2.5	+1.37	0.52	0.20	4.91	−0.11	0.41	0.05	6.65
W_{13}	s,p,d	3.0	+0.29	0.59	0.36	4.76	−0.02	0.50	0.09	5.43
		2.5	+1.08	0.54	0.27	4.11	−0.09	0.52	0.14	5.43

[a] s,p,d densities and the effective charge q are given for two values of R within a reasonable range. [b] For Pd_{13}, the p^x occupation is found to be negative ($x < 0$), which is physically meaningless and is an artifact of the Mulliken-type population analysis.

Though the interrelations between m and n (eq 2′–4′) may not be as simple as that between a and b (eq 6 and 7), the basic conclusion remains the same; namely, one should expect a crossover of the q_c and q' curves which, according to the inequalities of eq 10 and 11, should take place somewhere near the p^3 and d^5 configurations, respectively.

Because the p^3 population is too high to be realistic for any metal (alkali, noble, or transition), the p contribution to the center–outer metal separation will always be $q_{sec}^- - q_{surf}^+$, though typically marginal as compared with the s and d ones (see below). The d contribution is clear for such extremes of d^D as $D \gg 5$ ($q_{sec}^+ - q_{surf}^-$) and $D \ll 5$ ($q_{sec}^- - q_{surf}^+$) but may be of either sign for $D \simeq 5$. For the transition metal electron configuration $s^S d^D$ we should, in principle, consider the "(sd)^x model", where x, the effective occupation number, EON, is defined as the ratio of the number of metal valence electrons ($N = S + D$) to the number of metal valence s and d orbitals (six). So, we have for x the following range

$$\tfrac{2}{3} \le x \le \tfrac{5}{3} \qquad (12)$$

where $^2/_3$ corresponds to the titanium group and $^5/_3$ to the platinum one.[12] Thus, one can anticipate that for alkali, noble, and group 6–8 transition metals the surface atoms should be typically more negative but for transition metals of group 4 and probably group 5 the interior, in particular the second-layer atoms, may be most negative.

Because the surface (outer) atoms have smaller ligancy than the bulk (center, inner) ones, the surface atomic orbitals will be rehybridized. Such a rehybridization, as it follows from the perturbation-theory arguments,[5-7] should result in an enrichment of the low-coordinated atoms by the orbital components of the lowest energy, i.e., in the higher d occupancy in most of the transition metals[16] unlike the s occupancy in the main group metals,[7] for Li, in particular. We will discuss these aspects in more detail later.

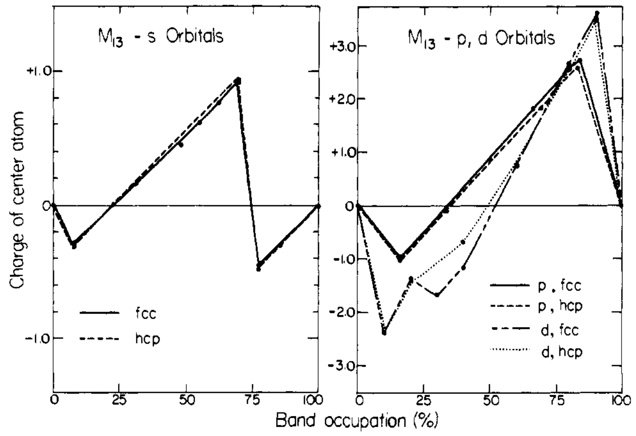

Figure 1. Dependences q_c vs. x for the s (a) and p and d (b) bands in fcc and hcp M_{13} electroneutral clusters. The 100% band occupation corresponds to s^2, p^6, d^{10} electron configurations of each metal atom. Equal (fictitious) nuclear charges maintain electroneutrality. See text.

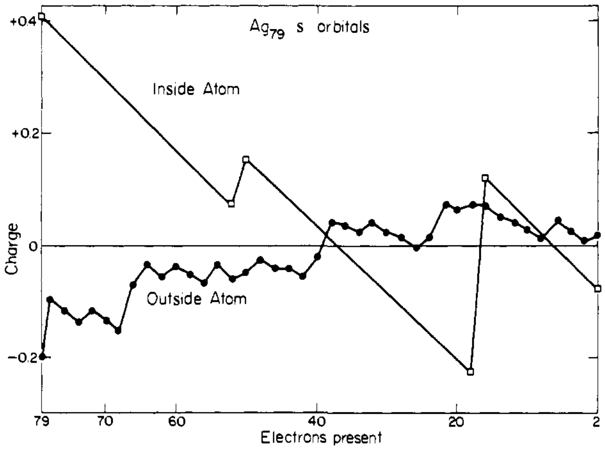

Figure 2. The charge of the center and an outside atom on electroneutral Ag_{79} fcc is plotted vs. the number of electrons added to the cluster. Only s orbitals are employed in the calculation, and the occupation number equals the number of electrons added divided by 79.

(2) Model (Cluster) Computations. To verify and clarify the above conclusions we have performed the EH and CNDO com-

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(14) (a) Selwood, P. W. "Chemisorption and Magnetization"; Academic Press: New York, 1975; p 12. (b) Anderson, J. R. "Structure of Metallic Catalysts"; Academic Press: New York, 1975; p 3.

(15) See, for instance, the discussion in (a) Mueller, F. M.; Priestley, M. G. *Phys. Rev.* **1966**, *148*, 638. (b) Ketterson, J. B.; Priestley, M. G.; Vuillemin, J. J. *Phys. Lett.* **1966**, *20*, 452.

(16) Namely, for the ending rather than for beginning transition metals such as Ti whose 4s orbital is slightly lower than the 3d ones.[17] Together with the electron deficiency ($x < 1$), it may result in the rather messy hybridization and charge distribution when, in particular, the second-layer sd orbitals rather than the surface ones will be the most occupied,[10] in agreement with the ab initio calculations on Ti(0001).[29]

(17) Ballhausen, C. J.; Gray, H. B. "Molecular Orbital Theory"; W. A. Benjamin: New York, 1965; p 122.

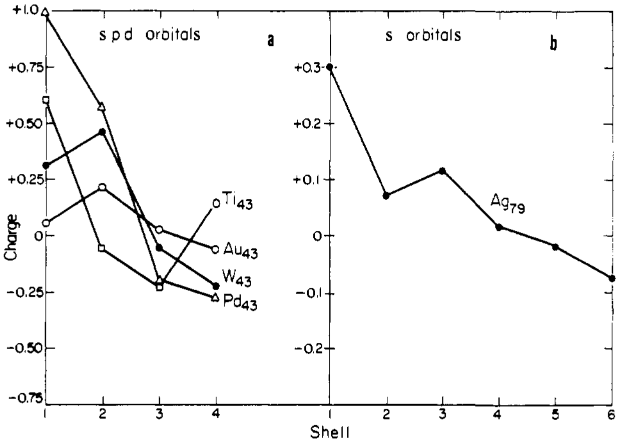

Figure 3. The charge of atoms in various shells in spherical fcc clusters is plotted vs. shell number for clusters of different occupancy and s, p, d (a) or s orbital (b) type. The shell number increases as the atom is placed further from the center.

putations on some model clusters. The results obtained are shown in Figures 1–3 and in Tables I and II.

First, we have confirmed the validity of the s^1 hypothesis (eq 5) for M$_{13}$. As seen from Table I, we really have the charge distribution $q_c > 0$, $q' < 0$.[18] There is a convenient way of representing q_c vs. x. We can assume some fictitious values of the initial nuclear charges to fit electroneutrality of the cluster for any x. In particular, for M$_{13}$ a negative slope of the plot q_c vs. x corresponds to filling of the A$_1$ (symmetric) MOs but a positive slope to filling of other (nonsymmetric) MOs. Obviously, the plot should be sinusoidal with one (positive) maximum but the number of (negative) minima and crossings will depend on the relative position of the antibonding MO ψ_1^* (eq 3). If ψ_1^* is the highest MO, the plot q_c vs. x will have one minimum and one crossing; if ψ_1^* is not the highest MO, this plot will have two minima and two crossings. In this way, we have analyzed the charge distribution in both fcc and hcp M$_{13}$ clusters for s, p, and d orbitals, individually, as shown in Figure 1. The different sinusoids for s, p, and d are distinctly seen, and the crossover points are found around the s$^{0.5}$, p^2, and d^5 populations, in accord with model expectations. Figure 2 depicts similar EH charges, both q_c and q_{outer}, for s orbitals of the fcc Ag$_{79}$ cluster.

In agreement with the s^1 model, Table I shows that, while going along the fcc series Ag$_{n+1}$, n = 12, 18, 42, 54, 78, first, the central atom charge (of the EH type) becomes less positive and even slightly negative and then again positive; second, though the charge distribution among the shells is nonmonotonic, the distribution $\delta_{\text{sec}}^+ - \delta_{\text{surf}}^-$ remains invariant except for M$_{19}$, as explained above[8] (see also Figure 3b). Substantially the same conclusions have been reached by the EH calculations on fcc M$_{43}$ clusters, M = Au, Pd, W, Ti, using the complete s, p, and d basis sets (Figure 3a). The EON values are $^{11}/_6$, $^5/_3$, 1, and $^2/_3$, respectively, for these clusters. Though the charge trends for atoms in the intermediate shells are nonmonotonic, the outer atoms in each of these clusters have negative charges except for Ti$_{43}$, as explained above.[10,16]

The s, p, d EH calculations on other fcc M$_{13}$ clusters, M = Cu, Ni, Pd, Pt, Rh, Ru, are summarized in Table II. In all the cases, except for Ni and Pd, $q_c > 0$, $q' < 0$. For the group 1 metal (Li, Cu, Ag) clusters MM'$_{12}$, where the s^1 model should be particularly appropriate, we always find, in agreement with ab initio calculations on Li$_n$ clusters,[20] the s density to be smaller on M than M' ($s_M^x < s_{M'}^x$). Further, in practically all the MM'$_{12}$ clusters the p density distribution has been found to be opposite ($p_M^x > p_{M'}^x$), again in accord with the ab initio calculations[20] and model expectations.[21]

For Ni$_{13}$ and Pd$_{13}$ we have $q_c < 0$, but $q_c > 0$ for Pt$_{13}$ (and other M$_{13}$). In the bigger clusters such as Ni$_{43}$[19] and Pd$_{43}$ (Figure 3a), the EH values of q_c are positive.

We have also performed the CNDO calculations on various M$_{13}$ clusters (M = Li, Ag, Pd) within the various basis sets (s, p, d).[19] Qualitatively, the CNDO results are similar to the EH ones.

Comparison with Other Approaches. From the studies dealing with problems of the bulk vs. surface charge distribution and rehybridization, we will briefly discuss only a few which are most important in the present context.

The s^1 hypothesis (eq 5) appears to be strict, but the s^1 model for clusters with nonequivalent ligands may give some variety of results. For instance, the ab initio HF s^1 calculations (assuming the spherically symmetric d^9 pseudopotential for Ni) on a fcc Ni$_{87}$ cluster[9a] have resulted in the charge distribution $q_c < 0$, $q_{\text{outer}} > 0$. It is not excluded, however, that this is an artifact of the HF approximation for such big clusters.[3b] Indeed, from the ab initio HF calculations on small clusters Li$_n$ of various geometries[20] it follows that the edge atoms all become slightly negative though they "always show less 2p admixture than the more central cluster atoms". Both of the above results for Li$_n$ perfectly agree with our model predictions.

The SCF–Xα–SW calculations on fcc M$_{13}$ clusters, M = Cu, Ni, Pd, Pt,[22] have also resulted in the charge distribution $q_c < 0$, $q_{\text{outer}} > 0$, namely, q_c = −0.518, −0.741, −0.748, and −0.935, respectively. But the Xα–SW calculations on C_{4v} M$_{13}$ clusters (M = Fe, Ni, Co)[23] show the opposite trend where "charge expansion from the center of the cluster to the edge atoms is a general feature". More important, the key conclusion[22] that the M$_{13}$ clusters are big enough to be bulklike definitely contradicts various size-dependent experimental findings.[24]

However, regardless of the accuracy of any numbers for the particular cluster M$_n$, the more important question remains of how to extrapolate these numbers from clusters to bulk metals. Remember that, in transition-metal solids, the d electrons are considered to be strongly localized, unlike the s and p electrons forming the electron sea.[3a] Thus, the cluster calculations where the s, p, and d electrons are considered on *equal footing* cannot be *directly* used for the cluster–solid extrapolations. Also, the contemporary solid-state models of transition metals strongly support the idea that the metal–metal bonding is mainly of the d–d character.[25]

Let us restate the main conclusions derived from our model: (1) the s and d contributions to the inner–outer metal charge separation are qualitatively similar (but typically opposite to the p contribution); (2) this separation will depend on the EON, i.e., show the crossover behavior. The qualitative similarity of conclusions derived from our s^1, (sd)^1, and (sd)^x models (considered in the context of the above basic solid-state notions) means, in fact, that one can expect the crossover behavior of the bulk vs. surface distribution of the transition metal d density.

To our knowledge, the only relevant experimental data to date are the bulk vs. surface atomic core binding energies measured for a series of the 5d transition metals.[26] Indeed, the surface-atom

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(18) Within the charge-noniterative EH procedure, a convenient way to distinguish between two possible charge separations, $\delta_M^+ - \delta_{M'}^-$ and $\delta_M^- - \delta_{M'}^+$, is to reach the zero separation, $\delta_M^0 - \delta_{M'}^0$, by decreasing or increasing, respectively, the center atom diagonal matrix element, H_{ii}, keeping outer-atom matrix elements unchanged. In the above Ag$_{13}$ case, such a zero separation has been reached by decreasing H_{ii} by 40%.[19]

(19) Baetzold, R. C., unpublished results (available upon request).

(20) Hermann, K.; Bagus, P. S. *Phys. Rev. B* **1978**, *17*, 4082.

(21) This result is related to the previous one concerning the opposing s and p contributions to the substituent effects in a variety of main-group and transition-metal compounds.[5-7]

(22) Messmer, R. P.; Knudson, S. K.; Johnson, K. H.; Diamond, J. B.; Yang, C. Y. *Phys. Rev. B* **1976**, *13*, 1396.

(23) Jones, R. O.; Jennings, P. J.; Painter, G. S. *Surf. Sci.* **1975**, *53*, 409.

(24) (a) Baetzold, R. C.; Mason, M. G.; Hamilton, J. F. *J. Chem. Phys.* **1980**, *72*, 366. (b) Unwin, R.; Bradshaw, A. M. *Chem. Phys. Lett.* **1978**, *58*, 58. (c) Roulet, H.; Mariot, J.-M.; Dufour, G.; Hague, C. F. *J. Phys. F* **1980**, *10*, 1025.

(25) See, for instance: (a) Pettifor, D. G. *Phys. Rev. Lett.* **1979**, *42*, 846. (b) Williams, A. R.; Gelat, C. D.; Moruzzi, V. L. *Phys. Rev. Lett.* **1980**, *44*, 429, and references cited therein.

(26) (a) Citrin, P. H.; Wertheim, G. K.; Bayer, Y. *Phys. Rev. Lett.* **1978**, *41*, 1425. (b) Duc, T. M.; Guillot, C.; Lassailly, Y.; Lecante, J.; Jugnet, Y.; Vedrine, J. C. *Phys. Rev. Lett.* **1979**, *43*, 789. (c) van der Veen, J. F.; Himpsel, F. J.; Eastman, D. E. *Phys. Rev. Lett.* **1980**, *44*, 189.

4f level has been found to be shifted (relative to the bulk value) to higher binding energy for Ta,[26c] but to lower binding energy for W,[26b] IR,[26c] and Au.[26a]

The straightforward bulk-surface computations also reproduce the above crossover behavior. For instance, the renormalized-atom model calculations on Ni[27] have shown "a flow of charge onto the surface site" reducing the d-hole count from its bulk value. Further, the latest ab initio (no pseudopotentials or other empirical forms are used) nine-layer calculations on the Cu(100)[28a,b] and Ni(100)[28c] surfaces reveal the edge bands predominantly of d-electron character, which is consistent with the core shift upward at the surfaces (as found for Au,[26a] Ir,[26c] and W[26b]). At the same time, the similar ab initio 11-layer calculations on Sc(0001) and Ti(0001) surfaces[29] predict the opposite sign for surface core shifts (as found for Ta[26c]), the occupancy of the surface states for Sc being smaller than that for Ti. All the above results agree with our model expectations.

Conclusion

We have to distinguish two aspects of the (sd)^x model, quantitative and qualitative. Quantitatively, the s^1, (sd)^1, and (sd)^x models may give rather different numbers. Qualitatively, these models lead to the similar conclusions concerning the surface vs. bulk charge distributions, showing very encouraging agreement with the known theoretical and experimental results. The main disagreement with other authors concerns the charge distributions in some particular model clusters. However, first, we are not interested in these hypothetical clusters themselves (but only as subject to extrapolations), and, second, the effective charge is not a well-defined property and cannot be directly observed and determined even in molecules,[30] not to mention the solids.[31] For this reason, some of the above contridictions may be a mere artifact of the concept used. We think that the best way to proceed is to compare the consequences of all model (computational) conclusions with various experimental (observable!) properties. These include energy and the density of states in the relevant two- and three-dimensional Brillouin zones as well as the differences in work functions[32] and other properties (first of all, catalytic activity) of different surfaces of the same metal, for instance, fcc (111), (110), (001), etc. We will discuss the application of our model to these aspects elsewhere.[10b,33]

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Appendix

Extended Hückel calculations[34] were performed in the standard manner, using the Wolfsberg–Helmholz formula for off-diagonal matrix elements with a constant value 1.75. Double ζ Slater orbitals were used to represent d orbitals with single Slater functions for the s and p. Standard parameters[35] were employed throughout, and the Mulliken-type analysis was used to determine the charge distribution. The CNDO calculations[36] were performed according to previous work.[37]

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(27) Fulde, P.; Luther, A.; Watson, R. E. *Phys. Rev. B* **1973**, *8*, 440.

(28) (a) Gay, J. G.; Smith, J. R.; Arlinghaus, F. J. *Phys. Rev. Lett.* **1979**, *42*, 332. (b) Smith, J. R.; Gay, J. G.; Arlinghaus, F. J. *Phys. Rev. B* **1980**, *21*, 2201. (c) Arlinghaus, F. J.; Gay, J. G.; Smith, J. R. *Phys. Rev. B* **1980**, *21*, 2055.

(29) (a) Feibelman, P. J.; Hamann, D. R. *Solid State Commun.* **1979**, *31*, 413. (b) Feibelman, P. J.; Appelbaum, J. A.; Hamann, D. R. *Phys. Rev. B* **1979**, *20*, 7433.

(30) See, for instance (a) Politzer, P.; Mulliken, R. *J. Chem. Phys.* **1971**, *55*, 5135. (b) Bader, R. F. W. *J. Am. Chem. Soc.* **1971**, *93*, 3095.

(31) Metal solids have the band structure (with the zero energy gap) whose occupancy is determined by the fixed Fermi level, which is the same for the bulk and all surfaces. Therefore, it is usually accepted that surface remains electroneutral, though an effective (electrostatic screening) potential of the surface atoms should be changed with respect to that of the bulk ones, mainly owing to the bulk vs. surface redistribution of the strongly localized d density (d holes).[26-29] Because the d redistribution seems to be rather insensitive to the s, p redistributions even in transition metal alloys,[25b] the former, we hope, can be treated in terms of effective charges.

(32) The differences in work functions for different surfaces cannot be explained by their effective charges only (whatever sign they would have!), but some polarization must be considered (in particular, the formation of the p-(sd) hybrid orbitals), creating a surface dipole moment.[10b]

(33) Baetzold, R. C.; Shustorovich, E., submitted to *Surf. Sci.*

(34) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 137.

(35) See, for instance, Baetzold, R. C. *J. Chem. Phys.* **1978**, *68*, 555.

(36) Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43S*, 129.

(37) Baetzold, R. C. *J. Chem. Phys.* **1971**, *55*, 4363.

Intrinsic Barriers in Nucleophilic Displacements

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Abstract: Measured rate constants and RRKM theory have been used to estimate central barrier heights in the double-minimum potential surfaces for several gas-phase S_N2 reactions. It is proposed that the barrier heights may be interpreted using the rate–equilibrium relationship originally developed by Marcus, and that the concept of intrinsic barriers embodied in this formalism can be useful when applied to nucleophilic displacements. The results are used to interpret alkoxide and fluoride nucleophilicities and leaving-group abilities.

Nucleophilic displacement reactions have been a fundamental part of organic chemistry for many years. Since the pioneering studies of Hughes and Ingold,[1] much effort has gone into kinetic studies of S_N2 reactions in the hope of developing structure–reactivity correlations. The Swain–Scott relation,[2a] the Edwards equation,[2b] and HSAB theory[2c] have all been used in attempts to correlate reactivity with structural or thermodynamic properties. Success of these correlations is rather limited, as absolute and even relative rates of S_N2 reactions have been found to be highly solvent

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(1) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, N.Y., 1969; p 422 ff.

(2) (a) Swain, C. G.; Scott, C. C. *J. Am. Chem. Soc.* **1953**, *75*, 141. (b) Edwards, J. D. *Ibid.* **1956**, *78*, 1819. (c) Pearson, R. G.; Songstad, J. *Ibid.* **1967**, *89*, 1827.

0002-7863/80/1502-5993$01.00/0