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A Study on Ni-H, Pd-H, and Pt-H Systems by Cluster Orbital Method

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As an application of the cluster orbitals proposed previously, nickel-, palladium-, and platinum-hydrogen systems are studied. Density of states, projected density of states, HOMO levels, and stabilization energies are calculated and compared with those obtained by extended Hückel method for small clusters. These calculations are extended to large clusters to find the size dependence of several physical quantities. Reduced overlap populations are also calculated to clarify the charge transfer phenomena reported earlier. The calculated physical quantities show no dependence on the cluster size. It is also found that the charge transfer occurs due to the intrinsic character of palladium, not due to the edge effect which may be present in small clusters.

Introduction

It has been reported previously[1], from extended Hückel (EH) calculations, that hydrogen atoms in palladium cluster are stabilized remarkably compared with those in nickel or platinum. It was also found that charge transfer from metal to hydrogen is more pronounced in palladium cluster than in nickel and platinum. These phenomena were interpreted as being either due to the intrinsic character of palladium or due to the edge effect which may be present in small

clusters. The clusters used for the calculations, however, were too small (with less than a hundred atoms) to show the edge effect properly. So it is necessary to consider large clusters to identify the possible edge effect which may be present in small clusters. Large clusters (say, clusters with more than a hundred or so atoms), however, cannot be treated by the EH method used earlier.

In the earlier work[2], it has been studied how to obtain analytic solutions of face-centered cubic (f.c.c.) clusters with arbitrary size. Though the shape of the clusters has been

restricted, their solutions could be obtained with cluster orbitals. All the metals studied previously (nickel, palladium, and platinum) are of f.c.c. structures (Hydrogen is assumed to be of f.c.c. structure). For these clusters, the cluster orbital method proposed earlier can be applied without cluster size limitation.

As the previous work[1], nine clusters - three metal clusters, three hydrogen clusters whose lattice parameters are identical with those of corresponding metals, and three combined (metal-hydrogen) clusters - are used for calculations. By calculating several physical quantities of these clusters, the changes which hydrogen experiences after it enters metal cluster are studied. The present work is focused on the cluster size dependence of various physical quantities to find the edge effect. Prior to these calculations, however, calculations are carried out for small clusters with the two methods - EH and cluster orbital methods.

Method

From the previous work[2], it has been found that analytic solutions of f.c.c. clusters could be obtained when their shapes satisfy some conditions. That is, the master (simple) cubic cluster of an f.c.c. one should be of rectangular parallelepiped shape and it has odd number of atoms along each axis (say, in case that the cubic cluster has N_A, N_B, and N_C atoms along x-, y-, and z-axes, N_A, N_B, and N_C should be odd numbers) and N_A, N_B, and N_C should be distinct (The condition that N_A, N_B, and N_C should be distint is dispensable[2].). The clusters which have been used earlier for the calculations of metal-hydrogen systems[1], however, do not satisfy these conditions. Thus, new clusters of the appropriate shape are needed in order to compare the cluster orbital and EH methods. EH calculations for these new clusters are carried out again and the results are compare with those obtained by cluster orbital method. Discussion in this section is confined only to cluster orbital method.

Figure 1 shows the shape of (a) metal, (b) hydrogen, and (c) metal-hydrogen clusters with $(N_A, N_B, N_C) = (7, 5, 3)$. All of nickel, palladium, platinum, and hydrogen are of f.c.c. structures (for hydrogen it is assumed), so it is possible to obtain their solutions with cluster orbitals. If the indices i, j, and k label the atom, all atoms with $j+j+k=$odd (or even) constitute an f.c.c. cluster. An f.c.c. cluster with $i+j+k=$odd is named as cluster I and one with $i+j+k=$even as cluster II. Since it does not matter whether $i+j+k$ is odd or even to obtain its solutions, two clusters (metal and hydrogen) may be either cluster I or II. For convenience, metal cluster is assigned arbitrarily to cluster I and hydrogen cluster to cluster II. Later, several clusters of various sizes will be treated. They are distinguished from each other with suitable size notations. The above clusters of $(N_A, N_B, N_C) = (7, 5, 3)$, for example, are named as $7 \times 5 \times 3$ clusters.

Now it is discussed how to obtain solutions of three $N_A \times N_B \times N_C$ clusters (metal, hydrogen, and metal-hydrogen ones) using cluster orbitals. For cluster I (metal), the solutions have already been obtained[2]. As mentioned earlier, a cluster orbital of ϕ-type (ϕ is one the nine atomic orbitals) for this cluster is defined as

$$\psi_{\phi}^{I, lmn} = N_0 \sum_{i,j,k}^{*} \phi(i, j, k) \sin i\xi \sin j\eta \sin k\zeta, \quad (1)$$
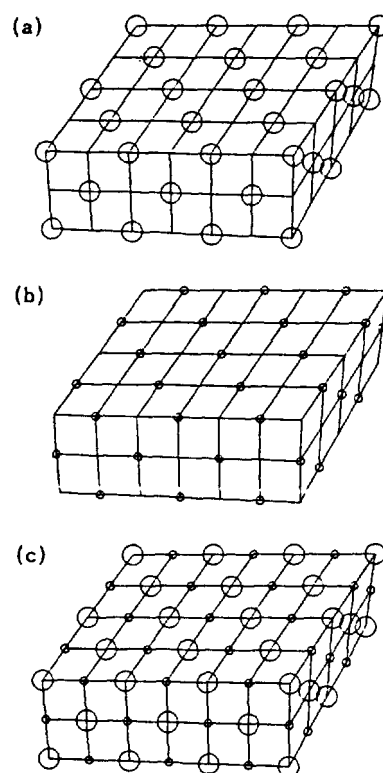

Figure 1. Shape of (a) metal, (b) hydrogen, mand (c) metal-hydrogen clusters (metal=Ni, Pd, and Pt) with $(N_A, N_B, N_C) = (7, 5, 3)$. Note that all these metals and hydrogen are of f.c.c. structures. Inner atoms are ommitted for the sake of simplicity.

where N_0 is the normalization constant

$$N_0 = [(N_A+1)(N_B+1)(N_C+1)/16]^{-1/2}. \quad (2)$$

ξ, η, and ζ are defined by

$$\xi = \frac{l\pi}{N_A+1}, \quad \eta = \frac{m\pi}{N_B+1}, \quad \zeta = \frac{n\pi}{N_C+1}. \quad (3)$$

l, m, and n are integers between 1 and N_A, N_B, and N_C repectively, and moreover they must satisfy the condition[3] $\xi + \eta + \zeta \leq 3\pi/2$. The superscirpt I of Eq. (1) represents that the cluster is of I-type ($i+j+k=$odd). The asterisk (*) of the summation denotes the restriction of $i+j+k=$odd. The Hamiltonian matrix composed of the elements which represent the interactions between any pairs of the cluster orbitals has the form shown in Figure 2(a). From the assumption made previously[2], all off-diagonal submatrices vanish. The form of one of the diagonal submatrices, only non-vanishing elements by the assumption, is given in Figure 2(b). Elements of this submatrix have been given previously[2]. Energies and wave functions (and other physical quantities) of the metal cluster may be found by diagonalizing these submatrices of nine by nine for N times (N is $(N_A N_B N_C+1)/2$, or the number of metal atoms).

For cluster II (hydrogen), a cluster orbital of h-type is defined as

$$\psi_{\phi}^{II, lmn} = N_0 \sum_{i,j,k}^{**} \phi(i, j, k) \sin i\xi \sin j\eta \sin k\zeta, \quad (4)$$

where the superscript II represents that the cluster is of

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(a)

$$(l_1, m_1, n_1) \ (l_2, m_2, n_2) \ (l_3, m_3, n_3) \cdots$$

(b)

(l, m, n)

(c)

(l, m, n)

Figure 2. (a) The form of the Hamiltonian matrix of metal cluster. By the assumption[2], only diagonal submatrices marked with "D" do not vanish. (b) One of the diagonal submatrices of (a) corresponding to state indices (l, m, n). s, x^2-y^2, $\cdots$ are not atomic orbitals but cluster orbitals of s-, x^2-y^2-, $\cdots$ types (type-I cluster orbitals). Cluster orbitals of only s-, x^2-y^2-, and z^2-types may mix from symmetry conditions. The Hamiltonian matrix of metal-hydrogen cluster is composed of $N-1$ diagonal submatrices of ten by ten and one diagonal submatrix of nine by nine. One of the diagonal submatrices of ten by ten is shown in (c), where h represents cluster orbital of h-type (type-II cluster orbital). Only four cluster orbitals (h-, s-, x^2-y^2-, and z^2-types) may mix by symmetry. The submatrix of nine by nine has the same form as that in (b) whose state indices are $((N_A+1)/2, (N_B+1)/2, (N_C+1)/2)$.

II-type ($i+j+k$=even). The asterisk prime (*') of the summation again denotes the restriction of $i+j+k$=even. This cluster orbital is that of hydrogen, so cluster orbitals of only one type, instead of nine types for metal, may be defined. It is, in fact, s-type but marked with h to avoid the ambiguity with s of metal. The Hamiltonian matrix of cluster II is composed of only $N-1$ diagonal elements. For hydrogen cluster the matrix is exact within the approximation of the cluster orbitals themselves (that is, overlaps are neglected and the interactions up to the second nearest neighbors are included[2,3]). The non-vanishing diagonal elements can be calculated similarly with the previous method[2] (within Hückel approximation including interactions up to the second nearest neughbors), say, as follows:

$$(h/h) \equiv <\psi_h{}^{ll, lmn}|H^{eff}|\psi_h{}^{ll, lmn}>$$

$$= E_{h, h}(000) + 4E_{h, h}(110)[\cos\xi\cos\eta + \cos\eta\cos\zeta$$

$$+ \cos\xi\cos\zeta] + 2E_{h, h}(200)[\cos 2\xi + \cos 2\eta + \cos 2\zeta]$$

$$+ 4E_{h, h}(200)\left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} + \frac{\sin^2\zeta}{N_C+1}\right]. \quad (5)$$

The combined cluster made up of metal atoms and hydrogen atoms in the interstices of them is composed of two interpenetrated f.c.c. clusters. Hamiltonian matrix may be set up with $9N$ cluster orbitals of I-type (for metal) and $N-1$ ones of II-type (for hydrogen). N diagonal submatrices of this matrix, only non-vanishing elements by the same assumption, are classified into two categories; $N-1$ submatrices of ten by ten and one submatrix of nine by nine. The submatrix of nine by nine arises since the number of hydrogen atoms is less by one than that of metal ones, so the cluster orbital of h-type is not defined for a state index. The state index, in reality, is $((N_A+1)/2, (N_B+1)/2, (N_C+1)/2)$ which is represented as (l_N, m_N, n_N), and only nine cluster orbitals may be defined for this state index. Figure 2(c) shows one of the $N-1$ submatrices of ten by ten. The submatrix of nine by nine corresponding to (l_N, m_N, n_N) has the same form as Figure 2(b), and the elements are the same, too. The only difference between them is the energy parameters, say $E_{s,s}(000)$, which are found from the Hückel matrix obtained by EH calculation. This point will be mentioned later. The submatrix of ten by ten [Figure 2(c)] represents interactions between any pairs of ten cluster orbitals-nine of type-I (for metal) and one of type-II (for hydrogen). The irreducible representation to which cluster orbitals of h-type (s-type of hydrogen) belong is the same as that to which cluster orbitals of s-, x^2-, and z^2-types belong. Cluster orbitals of only h-, s-, x^2-y^2-, and z^2-types, therefore, may mix in a given submatrix from the symmetry condition given earlier[2]. The submatrix is divided into a block of four by four and six diagonal elements. The elements whose forms are not found yet are (h/s), (h/x^2-y^2), (h/z^2), (s/h), (x^2-y^2/h), and (z^2/h). Since the submatrix is symmetric, it is sufficient to find the forms of only three elements among them. Within Hückel approximation they can be found, taking interactions up to the second nearest neighbors. They are given in Table 1.

To find the numerical values of the Hamiltonian matrix elements of these three clusters (in fact, nine clusters - three metal, three hydrogen, and three combined ones) and to cal-

Table 1. Some Elements of Diagonal Submatrices of Metal-hydrogen Cluster for a Given State Index[a]

$$(h/h)^b = E_{k,k}(000) + 4E_{k,k}(110)^c[\cos\xi\cos\eta + \cos\eta\cos\zeta + \cos\zeta\cos\xi]$$
$$+ 2E_{k,k}(200)[\cos2\xi + \cos2\eta + \cos2\zeta]$$
$$+ 4E_{k,k}(200)\left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} + \frac{\sin^2\zeta}{N_C+1}\right]$$

$$(h/s)^d = (s/h) = 2E_{k,s}(100)^c[\cos\xi + \cos\eta + \cos\zeta]$$
$$+ 8E_{k,k}(111)\cos\xi\cos\eta\cos\zeta$$

$$(h/x^2-y^2) = (x^2-y^2/h) = 2E_{k,x^2-y^2}(100)[\cos\xi - \cos\eta]$$
$$+ 8E_{k,x^2-y^2}(111)\cos\xi\cos\eta\cos\zeta$$

$$(h/z^2) = (z^2/h) = 2E_{k,z^2}(100)[\cos\xi + \cos\eta] + 2E_{k,z^2}(001)\cos\zeta$$
$$+ 8E_{k,z^2}(111)\cos\xi\cos\eta\cos\zeta$$

[a] Other elements are listed in Table 3 of ref. (2). [b] $(h/h) \equiv <\psi_h^{\text{ll},lmn}|H^{\text{eff}}|\psi_h^{\text{ll},lmn}>$. [c] $E_{k,k}(110) \equiv <h(i,j,k)|H^{\text{eff}}|h(i+1,j+1,k)>$. [d] $(h/s) \equiv <\psi_h^{\text{ll},lmn}|H^{\text{eff}}|\psi_s^{\text{L,bmn}}>$. [e] $E_{k,s}(100) \equiv <h(i,j,k)|H^{\text{eff}}|s(i+1,j,k)>$.

Table 2. Extended Hückel (EH) Parameters for Ni, Pd, Pt, and H

Orbital		[a]H_{ii} (ev)	[b]H_{ii} (ev)	ζ_1	ζ_2	C_1	C_2
	4s	−7.91	−8.33	1.925			
Ni	4p	−3.71	−4.10	1.925			
	3d	−10.16	−10.51	5.75	2.20	0.5817	0.5800
	1s[c]	−13.6	−10.92	1.3			
	5s	−6.58	−7.57	2.190			
Pd	5p	−0.29	−1.20	2.152			
	4d	−9.43	−11.13	5.98	2.613	0.5535	0.6701
	1s	−13.6	−10.80	1.3			
	6s	−8.86	−9.38	2.554			
Pt	6p	−4.23	−4.56	2.554			
	5d	−10.67	−11.47	6.013	2.696	0.6336	0.5513
	1s	−13.6	−11.81	1.3			

Parameters for [a] separate clusters (metal and hydrogen) and for [b] combined clusters. [c] 1s is 1s orbital of hydrogen.

Table 3. Comparison of HOMO Levels (in eV) Obtained by Cluster Orbital Method with Those by EH Calculations for 5×5 ×3 Clusters

	Ni		Pd		Pt	
	EH[a]	CO[b]	EH	CO	EH	CO
M_{38}	−9.506	−9.091	−8.899	−8.530	−9.796	−9.209
H_{37}	−13.312	−13.051	−13.424	−13.238	−13.431	−13.250
$M_{38}H_{37}$	−9.490	−9.220	−9.452	−8.842	−10.118	−9.447

HOMO levels from [a] EH calculation and [b] cluster orbital method.

Table 4. Differences of HOMO Levels for Hydrogen Clusters Calculated by the Two Methods vs. Lattice Parameters of the Metals

	Differences of HOMO levels (eV)	Lattice parameters (Å)
Ni	0.261	3.52
Pd	0.186	3.89
Pt	0.181	3.92

culate various physical quantities of the clusters, the numerical values of energy parameters mentioned earlier are needed. They may be obtained from Hückel matrices obtained by EH calculations. Extended Hückel parameters for these calculations are given in Table 2 and lattice parameters of three metals (and three corresponding hydrogens) are given in Table 4. In Table 2, parameters of two types are listed. Parameters of one type are those corresponding to separate clusters and those of the other type to combined clusters. Now the task is to calculate numerical values of each element of nine Hamiltonian matrices and to diagonalize them to obtain several physical quantities.

Cluster Orbital Approaches vs. Extended Hückel Calculations

To compare the physical quantities obtained by the two methods, nine 5×5×3 clusters are treated. Figure 3 shows density of states (DOS) of nickel (a), hydrogen (c), and nickel-hydrogen (b) clusters and DOS projected onto nickel (a) and hydrogen (c) of nickel-hydrogen cluster. All the curves with prime, say (a'), are the results of cluster orbital method and the others are those of EH method. Figures 4 and 5 show the same curves for palladium and platinum, respectively. By comparing each cooresponding curves, say Figure 3(a) with (a'), rough consistency between each pair is observed except DOS and PDOS of hydrogen. In case of hydrogen, (c) and (c') of Figures 3-5, ordinate scales are magnified for closer look and the differences are relatively exaggerated. The main differences between each pair arise from two reasons: (1) The off-diagonal submatrices representing interactions between cluster orbitals with different state indices are assumed to vanish[2], and (2) overlap integrals are neglected[3] in cluster orbital method. In hydrogen, the Hamiltonian matrix has no off-diagonal elements and the results differ from each other only because of neglecting overlap integrals. This matter will be quantitively discussed later. From (a)'s and (a')'s of Figures 3-5, the energy levels of palladium is much lowered than the other metals by the both methods, which may explain the largest stabilization of hydrogen in palladium reported earlier[1].

HOMO levels obtained by the two methods for these nine clusters are given in Table 3. There are some differences, about 0.2-0.6 eV, between the values obtained by the two methods. It was mentioned in last paragraph why they differ. To reveal the reason of the differences more quantitatively, the differences of HOMO levels of three hydrogen clusters calculated by the two methods are listed in Table 4 with the lattice parameters of the three clusters. It may reasonably be thought that the larger the difference is as the larger the overlap integrals between near atoms. The overlap integrals are smaller as the distance between atoms increases, or as the lattice parameter increases. Table 4 shows this. It is hopefully expected, then, that the differences may be overcome by considering overlap integrals[4]. In case of metal
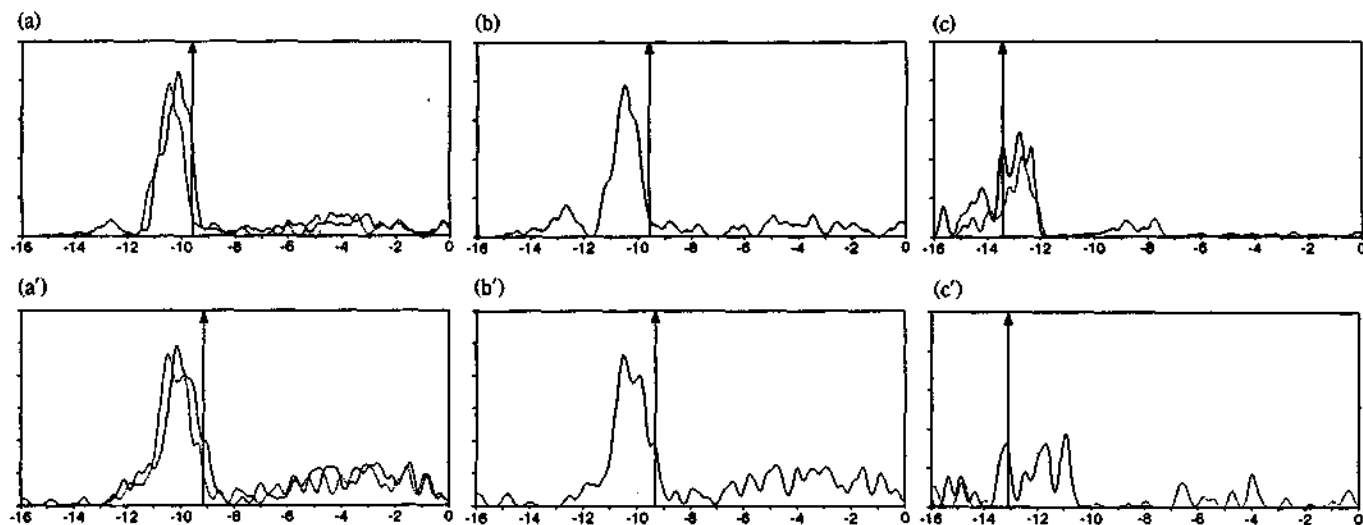
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Figure 3. (a) DOS of Ni_{38} cluster (solid line) and DOS projected onto Ni of $Ni_{38}H_{37}$ cluster (dotted line). (b) DOS of $Ni_{38}H_{37}$ cluster. (c) DOS of H_{37} cluster (solid line) and DOS projected onto H of $Ni_{38}H_{37}$ cluster (dotted line). All curves of (a')-(c') are the results obtained by cluster orbital method and those of (a)-(c) by EH method. Abscissa shows energy in eV, ordinate DOS (and PDOS) in arbitrary unit for each curve. Ordinate scales for (c) and (c') (for hydrogen) are magnified for closer look. Vertical arrows show HOMO levels of (a) nickel, (b) nickel-hydrogen, and (c) hydrogen clusters. For the numerical values of them, see Table 3.
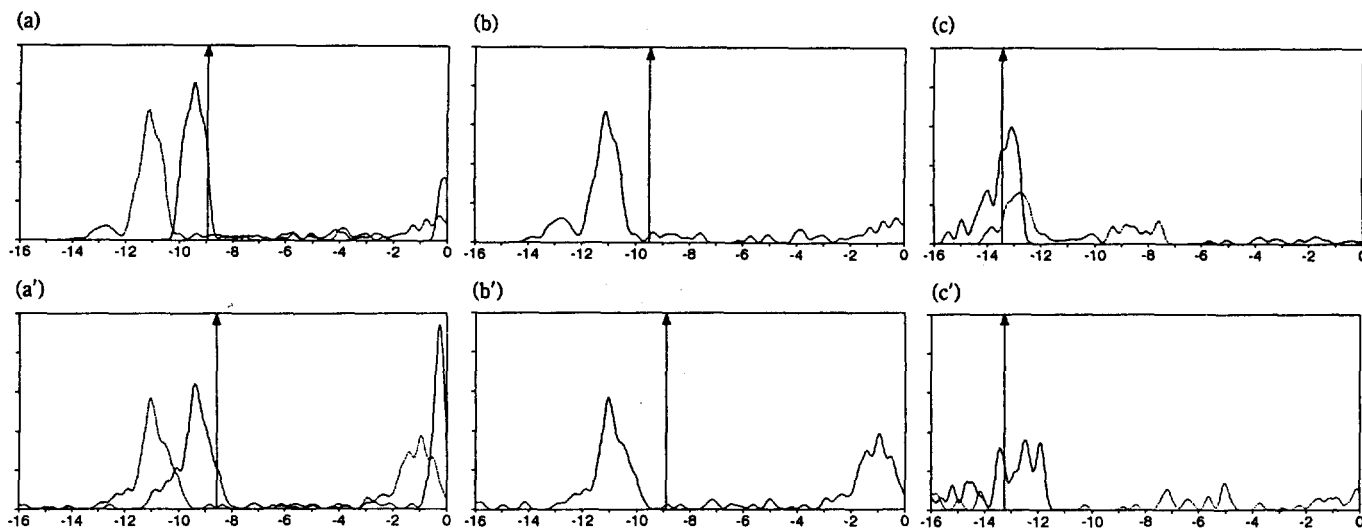

Figure 4. (a) DOS of Pd_{38} cluster (solid line) and DOS projected onto Pd of $Pd_{38}H_{37}$ cluster (dotted line). (b) DOS of $Pd_{38}H_{37}$ cluster. (c) DOS of H_{37} cluster (solid line) and DOS projected onto H of $Pd_{38}H_{37}$ cluster (dotted line). All curves of (a')-(c') are the results obtained by cluster orbital method and those of (a)-(c) by EH method. Ordinate scales for (c) and (c') (for hydrogen) are also magnified for closer look. Vertical arrows show HOMO levels at each curve.

or metal-hydrogen clusters, on the other hand, the differences occur by the assumption of non-vanishing off-diagonal elements as well as the neglect of overlap integrals. The differences may also be reduced to some extent by considering overlap integrals. In this work the two assumptions are made in calculation (no overlap integrals are included). Nevertheless the trend of the HOMO levels found by the two methods is consistent is spite of the numerical inconsistency. In fact, the values obtained by the cluster orbital method is always a bit higher than those by EH method and it is possible to compare the HOMO levels of the three metals even with the cluster orbital method.

From the previous work[1], it has been shown that hydrogen

atoms are more stabilized after insertion into palladium than into nickel or platinum. To find that it is the case by cluster orbital method, stabilization energies (S.E.) are calculated by the two methods. Total S.E. is defined as the difference between the sum of the total energies of metal and hydrogen clusters and the total energy of metal-hydrogen cluster. The value divided by the number of hydrogen atoms is the unit S.E. which represents how much a hydrogen atom is stabilized after entering metal cluster. These values are given in Table 5. There are considerably large differences between the results by the two methods. In this case, nevertheless, the largest stabilization of hydrogen atoms are found in palladium. This high stabilization of hydrogen in palladium may
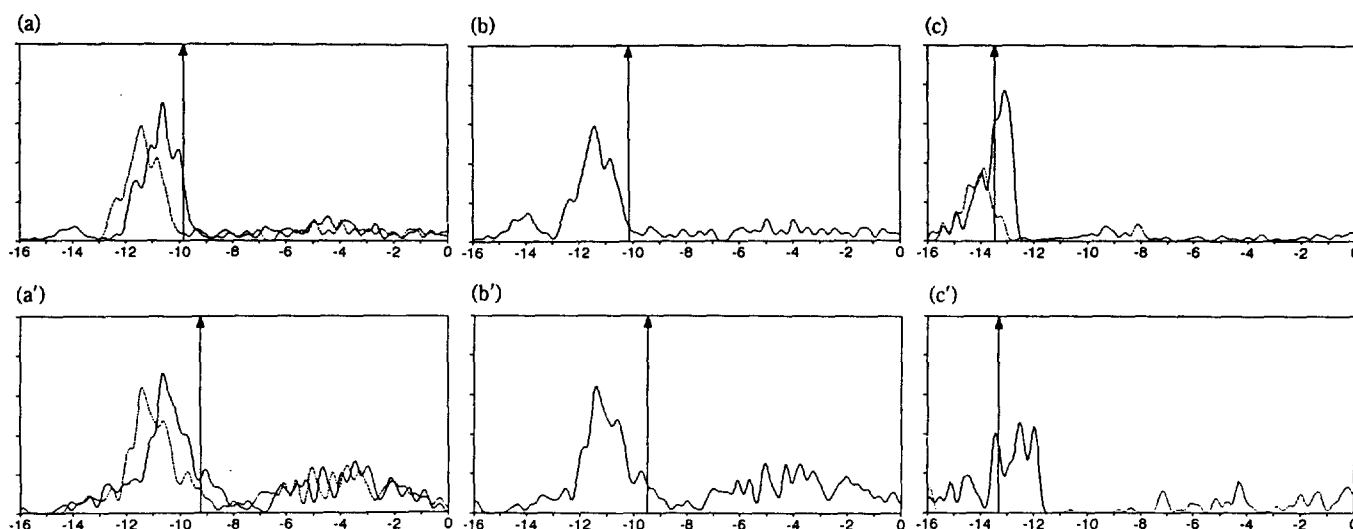
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(a)   (b)   (c)

(a')   (b')   (c')

Figure 5. (a) DOS of Pt_{38} cluster (solid line) and DOS projected onto Pt of $Pt_{38}H_{37}$ cluster (dotted line). (b) DOS of $Pt_{38}H_{37}$ cluster. (c) DOS of H_{37} cluster (solid line) and DOS projected onto H of $Pt_{38}H_{37}$ cluster (dotted line). All curves of (a')-(c') are the results obtained by cluster orbital method and those of (a)-(c) by EH method. Ordinate scales for (c) and (c') (for hydrogen) are magnified.

Table 5. Comparison of Stabilization Energies (S.E., in eV) of Hydrogen Calculated by the Two Methods

	Ni		Pd		Pt	
	EH[a]	CO[b]	EH	CO	EH	CO
$M_{38}(A)$[c]	−3,894.03	−4,113.41	−3,593.79	−3,716.88	−4,106.99	−4,306.35
$H_{37}(B)$[d]	−528.87	−564.46	−520.46	−536.12	−519.88	−534.32
$M_{38}H_{37}(C)$[e]	−4,547.70	−5,224.12	−4,736.00	−5,276.34	−4,959.28	−5,604.12
total S.E.[f]	−124.80	−546.25	−621.75	−1,023.34	−332.41	−763.45
unit S.E.[g]	−3.37	−14.76	−16.80	−27.66	−8.98	−20.63

S.E. from [a]EH and [b]cluster orbital methods. In the upper three rows, total energies (in eV) of [c]metals, [d]hydrogens, and [e]their combined clusters are listed. [f](total S.E.)≡ $C−(A+B)$; [g](unit S.E.)≡ (total S.E.)/(number of hydrogen atoms).

be understood from DOS and PDOS curves of Figure 4. From discussions up to now, it is found that DOS (and PDOS) curves, HOMO levels, and S.E. obtained by cluster orbital method are similar, at least qualitatively, with those by EH method.

Change of Physical Quantities with Cluster Size

The main concern in the present work is the cluster size dependence of various physical quantities. In this section, two quantities (HOMO levels and stabilization energies) are calculated for clusters with varying sizes. It has been shown, in the previous section, that the physical quantities calculated by cluster orbital method have the same trend as those by EH method, though the two results may lack in quantitative consistency. HOMO levels and stabilization energies of clusters, therefore, are calculated by cluster orbital method.

HOMO levels are given in Table 6 for three metal clusters, a hydrogen cluster whose lattice parameter is identical with that of nickel, and a nickel-hydrogen cluster with changing sizes. Those for other clusters are not presented for the pattern is similar. The Table shows that the HOMO levels are not changed much even if the size of clusters increases.

In order to show this more visually, changes of HOMO levels with cluster sizes (in logarithmic scale with base e) for palladium and nickel-hydrogen clusters (arbitrarily selected) are given in Figure 6. It may be seen, from this Figure, that HOMO levels converge as the cluster size increases.

Unit stabilization energies, defined in the previous section, of hydrogen in nickel, palladium, and platinum are given in Table 7 for clusters with varying size. They also converge and hydrogen in palladium is most stable for clusters of all size. It is, therefore, due to the intrinsic character of palladium not to the edge effect of small clusters, that the hydrogen in palladium is the most stable.

Reduced Overlap Populations

Reduced overlap population (ROP) is also, of course, a sort of physical quantity, but discussion on it is made in a separate section for two reasons. First, ROP is related to the charge transfer phenomena which have been the chief controversy of the previous paper[1]. And inconsistency between the two methods - cluster orbital and EH methods - arises in case of ROP, for overlaps are not included in cluster orbitals[3]. ROPs are defined as follows:

Table 6. HOMO Levels (in eV) of Several Clusters with the Change of Their Sizes

N_A	N_B	N_C	Number of metal atoms[a]	Ni[b]	H(Ni)[c]	NiH[d]	Pd[e]	Pt[f]
7	5	3	53	−9.07392	−13.01072	−9.14738	−8.49820	−9.29295
9	7	5	158	−9.04482	−12.59586	−8.95867	−8.42844	−9.16434
11	9	7	347	−9.00376	−12.54770	−8.97943	−8.36237	−9.13359
13	11	9	644	−8.98088	−12.54763	−8.94885	−8.33817	−9.12667
15	13	11	1,073	−8.96804	−12.51679	−8.94578	−8.33541	−9.11459
17	15	13	1,658	−8.95814	−12.52333	−8.93775	−8.32153	−9.10859
19	17	15	2,423	−8.95733	−12.53166	−8.93438	−8.31526	−9.08946
21	19	17	3,392	−8.95367	−12.49906	−8.93082	−8.30780	−9.08558
23	21	19	4,589	−8.95027	−12.48179	−8.92696	−8.29795	−9.07646
25	23	21	6,038	−8.94450	−12.46567	−8.92717	−8.29592	−9.07511

[a](number of metal atoms)=$(N_A N_B N_C + 1)/2$. The number of hydrogen atoms are less by one than that of metal atoms. HOMO levels of [b]nickel cluster, [c]hydrogen cluster whose lattice parameter is identical with that of nickel, and [d]combined (nickel-hydrogen) cluster. HOMO levels only of metal clusters are listed for [e]palladium and [f]platinum.
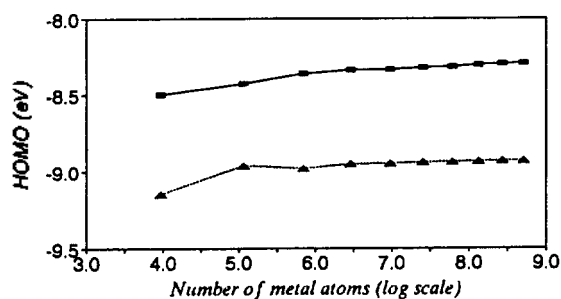

Figure 6. Change of HOMO levels with the number of metal atoms (in logarithmic scale with base e) for palladium (upper, solid line with rectangles) and nickel-hydrogen clusters (lower, dotted line with triangles).

$$P_{AA} = \sum_{i \in A} \sum_k n_k C_{ki}^2, \qquad (6)$$

$$P_{AB} = \sum_{i \in A} \sum_{j \in B} \sum_k n_k C^*_{ki} S_{ij} C_{jk}, \qquad (7)$$

where S_{ij} is (i, j) element of overlap matrix. From the definitions, P_{AA} can be thought to be the electron desity of atom A, P_{AB} divided by two the bond order between atoms A and B.

Various ROP values obtained by the two methods are given in Table 8. In this Table, P_{AA}'s are averaged values for metal or hydrogen atoms. P_{AB} cannot be averaged, for it is interatomic nature, so P_{AB}'s are taken from the center of each cluster. By EH calculations, it is found that hydrogens in palladium cluster lose their electrons less than those in nickel and palladium clusters from ΔP_{AA}(H) values of sub-table C. ROPs calculated by the two methods, however, cannot be compared directly with each other, for P_{AB} is always zero (because of neglecting overlap integrals) in case of cluster orbital method. The results of EH calculation show that both metals and hydrogens lose their electrons and these electrons are used to make bonds between each metal atoms and hydrogens. By the results of cluster orbital calculations, however, hydrogens lose their electrons and these electrons are not used to make bonds but to increase the electron

Table 7. Unit Stabilization Energies of Hydrogen (in eV) in Ni, Pd, and Pt with the Change of Their Sizes

Number of metal atoms	Ni	Pd	Pt
53	−15.18	−27.48	−21.07
158	−15.38	−27.46	−21.24
347	−15.57	−27.58	−21.41
644	−15.66	−27.66	−21.52
1,073	−15.72	−27.72	−21.60
1,658	−15.77	−27.76	−21.65
2,423	−15.81	−27.79	−21.69
3,392	−15.84	−27.81	−21.72
4,589	−15.86	−27.84	−21.75
6,038	−15.88	−27.85	−21.77

densities of metals (Since there are no electrons in bond regions, it is natural the other atoms get electrons if some atoms lose their electrons). Though it is not possible for the results calculated by the two methods to be compared with each other, it may be seen that the trend is unchanged. That is, hydrogens in palladium lose their electrons less than those in nickel and platinum by cluster orbital calculations, too.

To find whether it is the case for large clusters, ROPs (P_{AA}'s) are calculated by cluster orbital method and their changes after hydrogen insertion are listed in Table 9. Averaged ROP changes slightly increase as the size of clusters increases. The trend, however, is consistent for large clusters, i.e., hydrogens in palladium cluster lose their electrons less than those in the other metal clusters regardless of cluster size. The charge transfer phenomena observed for small clusters, therefore, are thought to arise not by the edge effect but by the intrinsic character of palladium. Table 10 represents ROPs and their changes for central atoms. The numbers of central metal atoms are 53 for clusters with odd number of metal atoms and 52 for clusters with even

Table 8. Reduced Overalap Population (ROPs) Obtained from M_{38} and H_{37} Clusters (A), $M_{38}H_{37}$ Clusters (B), and their Differences (C) with the two Methods

		Ni		Pd		Pt	
		EH[a]	CO[c]	EH	CO	EH	CO
A	$P_{AA}(M)$[e]	9.5923	10.0	9.8414	10.0	9.4760	10.0
	$P_{AA}(H)$	.9320	1.0	.9543	1.0	.9558	1.0
	$P_{AB}(M-M)$[d]	.1066	—[c]	.0290	—	.1597	—
	$P_{AB}(M-H)$	.0	—	.0	—	.0	—
	$P_{AB}(H-H)$	.0107	—	.0073	—	.0071	—
B	$P_{AA}(M)$	9.4368	10.0884	9.6368	10.0619	9.3967	10.0897
	$P_{AA}(H)$	.7200	.9092	.8234	.9364	.7217	.9079
	$P_{AB}(M-M)$	.0498	—	.0025	—	.0641	—
	$P_{AB}(M-H)$	.1221	—	.0838	—	.1176	—
	$P_{AB}(H-H)$	.0001	—	.0008	—	−.0001	—
C[f]	$\Delta P_{AA}(M)$	−.1555	+.0884	−.2046	+.0619	−.0793	+.0897
	$\Delta P_{AA}(H)$	−.2120	−.0908	−.1309	−.0636	−.2341	−.0921
	$\Delta P_{AB}(M-M)$	−.0568	—	−.0265	—	−.0956	—
	$\Delta P_{AB}(M-H)$	+.1221	—	+.0838	—	+.1176	—
	$\Delta P_{AB}(H-H)$	−.0106	—	−.0065	—	−.0072	—

Values obtained by [a]EH and [b]cluster orbital methods. [c]P_{AA}'s are averaged values for 38 metal atoms and for 37 hydrogen atoms. [d]P_{AB} cannot be averaged since it is interatomic nature, so P_{AB}'s are taken from the center of each cluster. [c]P_{AB}'s cannot be calculated with cluster orbital method, for overlaps are neglected. [f]This sub-table is constructed by the differences between A and B.

Table 9. Changes of Averaged ROPs of Metal and Hydrogen Atoms for Ni, Pd, and Pt with the Change of Cluster Size

Number of metal atoms	Ni		Pd		Pt	
	Ni[a]	H[b]	Pd	H	Pt	H
53	+.09007	−.09180	+.06413	−.06537	+.09071	−.09225
158	+.10175	−.10240	+.07086	−.07132	+.10043	−.10107
347	+.10964	−.10996	+.06884	−.06904	+.10397	−.10427
644	+.11402	−.11420	+.06892	−.06902	+.10382	−.10399
1,073	+.11738	−.11749	+.07236	−.07243	+.10449	−.10459
1,658	+.11838	−.11845	+.07460	−.07464	+.10753	−.10760
2,423	+.11917	−.11922	+.07529	−.07532	+.10929	−.10933
3,392	+.12074	−.12077	+.07600	−.07602	+.11172	−.11175
4,589	+.12123	−.12126	+.07655	−.07657	+.11202	−.11204
6,038	+.12191	−.12193	+.07710	−.07711	+.11232	−.11234

Changes of averaged ROPs of [a]nickel and [b]hydrogen after hydrogen enters nickel cluster.

number of metal atoms. Those of central hydrogen atoms are 52 and 53, respectively. The table shows that ROPs averaged over central atoms are lower than those averaged over all atoms for 7×5×3 cluster (10.0 for metal and 1.0 for hydrogen clusters, identical with the number of valence electrons). These are consistent with the fact that electrons are more dense at surface than at center[5]. ROP changes show the same trend. It follows that hydrogens in palladium also lose their electrons less even for central atoms (they are not affected by surface for large enough clusters, i.e., this is the case edge effect is nearly eliminated). This convinces the statement that the charge thransfer phenomena occur by the intrinsic character of palladium, not by the edge effect.

All calculations of ROPs are based on Mulliken population analysis[6]. To find the electron distributions more fully, in case of cluster orbital method, overlap should not excluded. It is claimed that cluster orbitals proposed previously and the assumption used for obtaining analytic solutions of f.c.c. clusters with them, produce results consistent, at least qualitatively, with those by EH calculations. If overlaps are involved, however, the results by the two methods show some differences, for overlaps are not included for cluster orbitals, especially in case of electron distributions. For the cluster orbital method to be used to find the electron distributions, therefore, new cluster orbitals including overlaps are needed and study on them is being carried out now and will be reported sooner or later[4].

Table 10. ROPs and Their Changes Averaged Over Central Atoms

Number of metal atoms[a]		M[b]	M (in MH)[c]	Changes[d]	H[e]	H (in MH)[f]	Changes[g]
53	Ni	10.00000	10.09007	+.09007	1.00000	.90820	−.09180
	Pd	10.00000	10.06413	+.06413	1.00000	.93463	−.06537
	Pt	10.00000	10.09071	+.09071	1.00000	.90755	−.09225
158	Ni	9.68975	10.07262	+.38287	.92301	.85400	−.06901
	Pd	9.68052	10.01485	+.33433	.92301	.88666	−.03635
	Pt	9.66632	10.05531	+.38899	.92301	.85851	−.06450
347	Ni	9.76002	9.96605	+.20603	.97607	.86817	−.10790
	Pd	9.69029	10.08239	+.39210	.97407	.90957	−.06450
	Pt	9.73448	9.93811	+.20363	.97407	.87704	−.09703
644	Ni	9.87024	9.97230	+.10206	.98948	.86654	−.12294
	Pd	9.81454	10.05567	+.24113	.98738	.90729	−.08009
	Pt	9.98128	9.96885	+.09757	.98738	.87645	−.11093
1,073	Ni	9.89303	10.06818	+.17515	.97221	.86456	−.10765
	Pd	9.87552	10.05442	+.17890	.97028	.90824	−.06204
	Pt	9.89560	10.04325	+.14765	.96962	.87788	−.09174
1,658	Ni	9.89727	10.08016	+.18289	.97741	.86740	−.11001
	Pd	9.86465	10.07551	+.21086	.97828	.90946	−.06882
	Pt	9.86180	10.04871	+.18691	.97882	.87794	−.10088
2,423	Ni	9.89387	10.07321	+.17934	.98565	.86598	−.11967
	Pd	9.87991	10.06960	+.18969	.98402	.90960	−.07442
	Pt	9.89285	10.04248	+.14963	.98402	.87771	−.10631
3,392	Ni	9.91958	10.07297	+.15339	.98530	.86698	−.11832
	Pd	9.89202	10.06703	+.17501	.98376	.91059	−.07317
	Pt	9.91805	10.05211	+.13406	.98345	.87638	−.10707
4,589	Ni	9.93189	10.07280	+.14091	.98596	.86765	−.11831
	Pd	9.91050	10.07285	+.16235	.98634	.91111	−.07523
	Pt	9.92295	10.06184	+.13889	.98565	.87753	−.10812
6,038	Ni	9.92962	10.08006	+.15044	.98378	.86785	−.11593
	Pd	9.92530	10.07221	+.14691	.98176	.91187	−.06989
	Pt	9.92596	10.07111	+.14515	.98297	.87778	−.10519

[a]The numbers of central metal atoms are 53 for clusters with odd number of metal atoms and 52 for clusters with even number of metal atoms. The number of central hydrogen atoms are 52 and 53, respectively. Net charges averaged over central metal atoms [b]in metal cluster and [c]in metal-hydrogen cluster and [d]their differences. Those averaged over central hydrogen atoms [e]in hydrogen cluster and [f]in metal-hydrogen cluster and [g]their differences.

Conclusion

Studies on palladium-hydrogen system have begun to reveal the cold fusion phenomenon[7] reported by Pons and Fleishmann. In the present work, our previous calculations are extended to large clusters with cluster orbital method. Form discussions up to now, some concluding remarks are collected.

1. With cluster orbital approach, various physical quantities can be calculated and they are not much different, at least qualitatively, from those obtained by EH calculations for small clusters.

2. The HOMO levels, stabilization energies, and reduced overlap populations do not change considerably as the cluster size increases.

3. The charge transfer phenomenon occurred for pallaidum is thought to be due to the intrinsic character of palladium, not to the edge effect of small cluster.

4. New cluster orbitals including overlaps are needed to see the more accurate electron distribution.

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Determination of Mono-, Di-, and Tri-Butyltin Compounds in Seawater of Several Bays in Korea

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The method of study describes the determination of the nanogram amounts of mono-, di-, and tri-butyltin compounds in sea water. The procedure is based on 1) the conversion of tin compounds to non-ionic species by sodium tetraethyl borate as an alkylation reagent, 2) one-step ethylation and 3) extraction. No further purification or concentration of the extract was required before GC-FPD (Flame Photometric Detector). The detection limits for mono-, di,- and tri-butyltin were 12.50, 6.02, and 4.19 ng/L. The linear range (0-120 ng/L) was solely dependent on the detector response height. Sea water samples (n = 24) were obtained from Masan Bay, Busan, Ullsan, Gunsan, Sockcho, Yeasu, Donghae, Inchun, Kanghwa, and Ahsan in Korea. The samples were collected between June, 1992 to July, 1992 and the distribution of monobutyltintrichloride (MBTC), dibutyltindichloride (DBTC), and tributyltinchloride (TBTC) in sea water was recorded. The concentrations of butyltin compounds in seawater were found to be in the range of N.D. (not detected)-61.93 ng/L for MBTC, N.D.-32.16 ng/L for DBTC, and N.D.-55.76 ng/L for TBTC.

Introduction

The production of butyltins has continuously increased on a worldwide basis in the last several decades (from under 5,000 tones in 1955 to at least 35,000 tones in 1992), due to the antifouling agent in paints for boats, submerged marine structure, and stabilizers for polyvinylchloride.

These butyltins chemicals have very high toxicity for some non-target species, particularly in estuaries near bays.[1] The toxicity of butyltine compounds is depend on the number of alkyl groups, of which alkyl group's number 3 and 4, are the most toxic.[2] Environmental degradation causes stepwise loss of organic groups from the Tin atom, which results in a variety of species, whith less toxicity. The toxicity of an individual species and the probability that a compound will be incorporated in the food chain is dependent on the nature of the alkyl group. Butyltins antifouling paints (TBT) have disturbed oyster farming.[3] Advance effects on growth and calcifications have been observed[4] and it is suspected that the fecundity of adult oysters has been affected.[5] Among the most visible effects is shell deformation of the oyster *Crassostrea virginica* and development of male sexual organs in the female dogwhelk *Nucella Lapillus*.[6] Pacific oyster reproduction is inhibited at areas with concentrations, about 20 ng/L for TBT.[7] Recently regulations in some countries re-

quire the limiting of TBT levels to no more than 1 ng/L in coastal sea water.

Current techniques for analysizing butyltins compounds in sea water are based in the use of chromatography with pre-column derivatization step,[8-12] ether by hydride generation[13] or by Grignard alkylation.[14] These techniques are time consuming and not entirely reliable. These procedures must be carried out in a clean, dry organic solvent and requires final clean-up and concentration. Hydride generation of volatile organotin compounds has been performed directly in aqueous environments, using sodium tetrahydro borate. However, organotin hydride compounds are very unstable and very volatile so that this lead to a loss of compounds and consequent underestimation of concentration. Therefore, sodium tetraethyl borate was used in this work for alkylation step.[15] Ethylation and extraction requires only one flask during the operation. The technique is as easy and quick as that use of sodium borohydrate and provides the same advantages as for alkyl derivative from the Grignard reaction. The reserches survey the principal bays of Korea and made a minute study for Masan Bay, by this method. The results are presented in Tables 1 and 2.

Experimental Section

Apparatus. A Hewlett Packard 5890II Gas Chromatogra-

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