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Modified Analytic Solutions of F.C.C. Metal Clusters

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By including the overlap integrals between atomic orbitals, the modified cluster orbitals for a metal cluster of face centered cubic lattice are found. The modified analytic solutions of the cluster are obtained from them with the assumption that the cluster orbitals with different state indices do not mix together. The physical properties—the HOMO levels and the unit electronic energies—of Ni, Pd, and Pt clusters of various size, calculated by the modified cluster orbital method, agree better with the results obtained by the Extended Hückel calculation than those of the previous (unmodified) cluster orbital method do. As a result, it is verified that the physical properties, at least those related to the energy levels, obtained by the Extended Hückel method may be reproduced by use of the modified cluster orbital method instead.

Introduction

The molecular orbitals and their energies of a face-centered cubic (f.c.c.) metal cluster were found, in the previous work,[1] from the cluster orbitals[2] of nine types (one *s*-, three *p*-, and five *d*-types) instead of atomic orbitals. In order to obtain the analytic solutions which are not limited to the cluster size, it was assumed that the cluster orbitals with different state indices do not mix together. Several physical properties for the metal-hydrogen systems have been calculated in this way[3] and it has been shown that the results agreed well, at least qualitatively, with those obtained by the Extended Hückel (EH)[4] calculation. Though the assumption we have made seemed to be somewhat nonsensical, there was no other way than neglecting the off-diagonal submatrices (the Hamiltonian matrx elements denoting the interactions between the cluster orbitals with different state indices); they could not be treated easily. It was expected,[1] however, that better results might be obtained with some modification of the scheme.

If only one atomic orbital (of any type) is allowed per site (per each atom), the solutions (the molecular orbitals and their energies) may be obtained analytically without any assumption such that the off-diagonal mixings do not occur.[2,5-7] The density of states (DOS), the HOMO levels, and the total electronic energies of the hypothetical hydrogen clusters of f.c.c. lattice calculated by the analytic (cluster orbital) method, however, did not accord well with the results obtained by the EH calculation. The main difference between the two results was thought to arise from neglecting the overlap integrals between atomic orbitals in case of the cluster orbital method. It is reasonably expected, therefore, that the difference may disappear, or at least be reduced, by including the integrals.

In this work the modified cluster orbitals of an f.c.c. metal cluster, including the overlap integrals explicitly, are found and the analytic solutions of the cluster are obtained from them with the same assumption that the off-diagonal mixings do not occur. Since the same assumption as the earlier work[1] is made, the problem of the treatment of the off-diagonal submatrices is not still solved; nevertheless the scheme has been modified. The molecular orbitals, however, are not treated in this article and only the orbital energies are calculated, *i.e.*, the concern is limited only to the physical properties related to the energy levels.

Modified Cluster Orbitals of F.C.C. Lattice

The shape of the f.c.c. metal cluster used throughout this article is the same as that of the earlier works:[1-3] it is of rectangular parallelepiped shape, whose master (simple) cubic cluster has N_A, N_B, and N_C atoms along x-, y-, and z-axes, respectively. Besides N_A, N_B, and N_C are all odd (and distinct). Then a modified f.c.c. cluster orbital of ϕ-type (ϕ is one of the nine atomic orbitals) is defined as[8]

$$\Psi_\phi^{lmn}=N_F\sum_{i,j,k}^{*}\phi(i,j,k)\sin i\xi\ \sin j\eta\ \sin k\zeta, \qquad (1)$$

where N_F is the normalization constant

$$N_F=[s_\phi^{lmn}(N_A+1)(N_B+1)(N_C+1)/16]^{-1/2}. \qquad (2)$$

ξ, η, and ζ are defined as previously[1] and the asterisk (*) on the summation is the restriction of $i+j+k=odd$ ($even$) for the cluster of type I (II)[3]. The modification, therefore, is that the factor s_ϕ^{lmn} is included in the normalization constant. s_ϕ^{lmn} is defined as

$$s_\phi^{lmn}\equiv<\Psi_\phi^{\mathrm{UM},lmn}|\Psi_\phi^{\mathrm{UM},lmn}>\equiv(\phi\cdot\phi), \qquad (3)$$

where $\Psi_\phi^{\mathrm{UM},lmn}$ denotes the earlier (unmodified) cluster orbital. In the previous paper,[1] the (unmodified) cluster orbital energy

$$<\Psi_\phi^{\mathrm{UM},lmn}|H^{eff}|\Psi_\phi^{\mathrm{UM},lmn}>\equiv(\phi/\phi) \qquad (4)$$

was obtained and (ϕ/ϕ)'s were tabulated. The quantity s_ϕ^{lmn} or $(\phi\cdot\phi)$ may be found from (ϕ/ϕ) by replacing E with S,[8] say

$$\begin{aligned}(z^2\cdot z^2)=1&+4S_{z2,z2}(110)\cos\xi\cos\eta\\&+4S_{z2,z2}(011)[\cos\eta\cos\zeta+\cos\xi\cos\zeta]\\&+2S_{z2,z2}(200)[\cos2\xi+\cos2\eta]+2S_{z2,z2}(002)\cos2\zeta\\&+4S_{z2,z2}(200)\left[\frac{\sin^2\xi}{N_A+1}+\frac{\sin^2\eta}{N_B+1}\right]\\&+4S_{z2,z2}(002)\frac{\sin^2\zeta}{N_C+1},\end{aligned} \qquad (5)$$

where $S_{z2,z2}(110)$ is an overlap integral between atomic orbitals

$$S_{z2,z2}(110)=<d_{z2}(i,j,k)|d_{z2}(i+1,j+1,k)> \qquad (6)$$

and $E_{z2,z2}(000)$ is replaced by $1=S_{z2,z2}(000)$. Thus the modified cluster orbital energy is

$$<\Psi_\phi^{lmn}|H^{eff}|\Psi_\phi^{lmn}>=(\phi/\phi)/(\phi\cdot\phi). \qquad (7)$$

Compared with the orbital energy given in Eq. (4), Eq. (7) has an additional factor which arises from including the overlap intergrals.

Before going further, the hypothetical hydrogen clusters studied earlier[3] are reexamined by the modified cluster orbital method. A hydrogen atom has only one electron in 1*s* orbital (in the ground state) and the hydrogen cluster may be treated by use of cluster orbital method, allowing only one atomic orbital per site (thus only one type of cluster orbitals). [For the present, 'cluster orbital' may be the previous (unmodified) cluster orbital or the modified cluster orbital. Both of them differ from each other only in their forms and they can be used similarly. When they are compared later, they will be discriminated from each other as the cluster orbital (C.O.) and the modified cluster orbital (M.C.O).] First, three hydrogen clusters composed of 52 H atoms (7×5×3 clusters of type II),[3] whose lattice parameters are identical with those of nickel, palladium, and platinum respectively, are taken into account. From 52 1*s* orbitals of H, 52 cluster orbitals, each of which is a linear combination of these atomic orbitals, may be found. These cluster orbitals are obtained by including the interactions up to the second nearest neighbors[1,2] and they are not, in reality, orthogonal to each other. To find the molecular orbitals and their energies, therefore, it is necessary to diagonalize the Hamiltonian matrix of 52×52. But it is not the aim of this work. One thing available for the simplification of the problem is that the terms representing the interactions between the cluster orbitals with different state indices (the off-diagonal elements of the Hamiltonian matrix) occur only between the second nearest neighbors; they go smaller and smaller as the cluster size increases[1]. The off-diagonal elements, therefore, are not included in the calculation and the cluster orbitals themselves constitute the molecular orbitals of the hydrogen cluster. The results are given in Figure 1 and Table 1. Figure

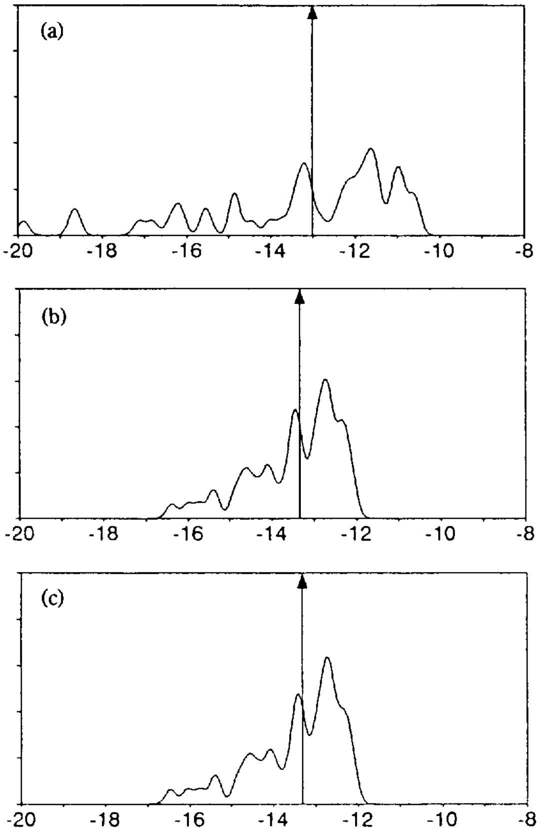


Figure 1. DOS curves of H_{52} cluster (7×5×3) obtained by (a) cluster orbital (C.O.), (b) modified cluster orbital (M.C.O), and (c) EH methods. The lattice parameter of this cluster is identical with that of nickel. Abscissa shows energy in eV, ordinate DOS in arbitrary unit. The vertical arrow of each curve shows the HOMO level found by each method. The numerical values of the HOMO levels are given in Table 1.

Table 1. HOMO Levels and Total Electronic Energies of Three Hypothetical Hydrogen Clusters Calculated by Three Methods (in eV)[a]

	Cluster	C.O.[b]	M.C.O.[c]	EH[d]
HOMO	H(Ni)[e]	−13.011	−13.342	−13.329
	H(Pd)	−13.256	−13.450	−13.444
	H(Pt)	−13.271	−13.457	−13.450
Total	H(Ni)	−788.28	−744.96	−744.15
Electronic	H(Pd)	−747.23	−732.42	−732.07
Energy	H(Pt)	−744.64	−731.50	−731.23

[a]Each cluster, of f.c.c. lattice, is composed of 52 hydrogen atoms (7×5×3 cluster of type II). The HOMO levels and total electronic energies obtained by [b]cluster orbital, [c]modified cluster orbital, and [d]EH methods. [e]Hydrogen cluster whose lattice parameter is identical with that of nickel.

Table 2. Comparison of the HOMO Levels and the Unit Electronic Energies of the Hydrogen Clusters (with the Lattice Parameter of Ni) with Varying Size Obtained by M.C.O. and EH Methods

Number of atoms	HOMO Level			Unit electronic energy[a]		
	M.C.O.[b]	EH[c]	Diff.[d]	M.C.O.[e]	EH[f]	Diff.[g]
22	−13.444	−13.420	−.024	−14.296	−14.280	−.016
37	−13.359	−13.312	−.047	−14.310	−14.294	−.016
52	−13.342	−13.329	−.013	−14.326	−14.311	−.015
67	−13.150	−13.154	+.004	−14.330	−14.315	−.015
94	−13.175	−13.177	+.002	−14.344	−14.330	−.014

[a]Unit electronic energy is defined as the total electronic energy divided by the number of atoms of each cluster. HOMO levels obtained by [b]M.C.O. and [c]EH methods and [d]their differences. Unit electronic energies obtained by [e]M.C.O. and [f]EH methods and [g]their differences.

1 shows the density of states (DOS) curves of H_{52} cluster, with the lattice parameter of Ni, obtained by three methods: cluster orbital (C.O), modified cluster orbital (M.C.O.), and EH methods. This Figure tells that the inconsistency between the results obtained by the C.O. and EH methods has been fully reduced, with the M.C.O. method being used instead of the C.O. method. Each vertical arrow in this Figure denotes the HOMO level. The HOMO levels are given in Table 1 quantitatively for the three clusters. It is remarkable that the difference of the HOMO levels obtained by the M.C.O. and EH methods is within 0.02 eV. The total electronic energies calculated by the three methods are also contained in the Table, and the results by the M.C.O. and EH methods do agree well. A bit of inconsistency between the two results are chiefly caused by the effect of the off-diagonal terms. As mentioned earlier, however, these terms will go smaller as the cluster size increases and it is expected that the difference will be reduced for larger clusters. Table 2 shows this: the HOMO levels and the unit electronic energies (the total electronic energies divided by the number of atoms)[3] of several H clusters (with the lattice parameter of Ni) with varying size, obtained by the M.C.O. and EH methods, are listed in this Table and the differences go smaller rapidly as the cluster size increases (The differences of the unit electronic energies do not go smaller *rapidly*, but the differences are too small.). Thus the modified cluster orbital energies of the hydrogen cluster agree very well with the molecular orbital energies of the cluster obtained by the EH calculation. In other words, the results of the EH calculation may be completely reproduced by the modified cluster orbital method, as long as only one atomic orbital is allowed per site.

Modified Analylic Solutions of F.C.C. Metal Clusters

More than one atomic orbitals being allowed on each site, the Hamiltonian matix is not so simple as that of the one-atomic-orbital case. To simplify the problem, the off-diagonal submatrices (the mixings between the cluster orbitals whose state indices are not identical with each other) are also neglected as previously.[1,9] Thus the modification in finding the analytic solutions is not an explicit, or more accurate, treatment of the off-diagonal submatrices but the use of the modified cluster orbitals. If the assumption of vanishing of the off-diagonal submatrices is accepted, the diagonalization of $9N\times 9N$ Hamiltonian matrix (N is the number of atoms in the cluster) is again reduced to the diagonalization of 9×9 matrix (In reality, the diagonalization of only 3×3 matrix is needed for the symmetry condition.[1]) for N times.

All the elements of a submatrix of 9×9 may be known: the other off-diagonal elements, except a 3×3 block, vanish by the symmetry condition[1] and the diagonal elements have been given by Eq. (7) in the previous section. The other non-vanishing off-diagonal elements can also be found:[1,8] $H_{s,z2}$, for example, is

$$H_{s,z2}\equiv <\Psi_s^{lmn}|H^{eff}|\Psi_{z2}{}^{lmn}> = (s/z^2)/[(s\cdot s)\,(z^2\cdot z^2)]^{1/2}, \tag{8}$$

where

$$\begin{aligned}(s/z^2) = {} & 4E_{s,z2}(110)\cos\xi\cos\eta + 4E_{s,z2}(011)[\cos\eta\cos\zeta + \cos\xi\cos\zeta] \\ & + 2E_{s,z2}(200)[\cos2\xi + \cos2\eta] + 2E_{s,z2}(002)\cos2\zeta \\ & + 4E_{s,z2}(200)\left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1}\right] \\ & + 4E_{s,z2}(002)\frac{\sin^2\zeta}{N_C+1},\end{aligned} \tag{9}$$

and

$$\begin{aligned}(s\cdot s) = 1 & + 4S_{s,s}(110)[\cos\xi\cos\eta + \cos\eta\cos\zeta + \cos\xi\cos\zeta] \\ & + 2S_{s,s}(200)[\cos2\xi + \cos2\eta + \cos2\zeta] \\ & + 4S_{s,s}(200)\left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} + \frac{\sin^2\zeta}{N_C+1}\right].\end{aligned} \tag{10}$$

$(z^2\cdot z^2)$ was given in Eq. (5). Thus all the non-vanishing elements of the diagonal submatrix (of 9×9) for a given state index (l, m, n) can be given. By numerical diagonalization, the molecular orbital energies of the cluster can be found from the eigenvalues. The molecular orbitals themselves may also be found from the eigenvectors, but they are not treated in this article.

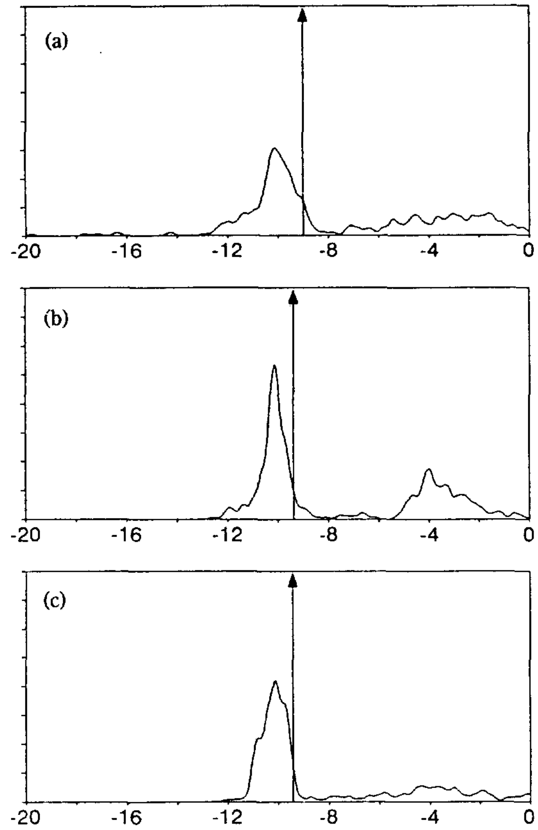


Figure 2. DOS curves of Ni$_{53}$ cluster (7×5×3) obtained by (a) cluster orbital (C.O.), (b) modified cluster orbital (M.C.O.), and (c) EH methods. Abscissa shows energy in eV, ordinate DOS in arbitrary unit. Vetical arrow shows the HOMO level found by each method.

Ni, Pd, and Pt Clusters: Comparison with the Results of EH Calculation

Nickel, palladium, and platinum clusters of f.c.c. lattice have been studied by the EH calculation[10] and with the cluster orbital (C.O.) method[3]. In this work, their DOS curves (energy levels), HOMO levels, and total electronic energies are calculated again by the modified cluster orbital (M.C.O.) method. Figure 2 shows the DOS curves of Ni$_{53}$ cluster (7×5×3 cluster of type I)[3] obtained by the three methods: (a) C.O., (b) M.C.O., and (c) EH methods. Each vertical arrow shows the HOMO level found by each method. The DOS curve obtained by the M.C.O. method has narrower bands than that by the C.O. method, which is caused by including the overlap integrals. However, it cannot be determined, merely from the DOS curves, whether any modification has been made or not. For a more quantitative description, the HOMO levels and the unit electronic energies of Ni, Pd, and Pt clusters with varying size—3×5×3 (23), 5×5×3 (38), 7×5×3 (53), 9×5×3 (68), and 5×5×5 (63) (The number in each parenthesis is the number of the metal atoms of each cluster.)—are tabulated in Table 3 and 4. The difference of the HOMO levels (Table 3) obtained by the C.O. and EH methods has been much reduced by using the M.C.O. method instead: the differences between the results by the M.C.O. and EH methods are within 0.2 eV or so. (Each HOMO level is visualized in Figure 3(a) for Ni clusters.) This difference is somewhat larger than that for the hydrogen clusters in spite of including the overlap integrals, for the off-diagonal submatrices are not still included. But a hopeful thing is that the results have been much modified nevertheless. Moreover the unit electronic energies (Table 4) obtained by the M.C.O. method agree very well with those by the EH calculation.

Table 3. Comparison of the HOMO Levels (in eV) of Various Meteal Clusters of Small Size Obtained by the Three Methods

Metal	Method	Number of atoms of each metal cluster[a]				
		23	38	53	68	63
Ni	C.O.[b]	−9.149	−9.091	−9.074	−9.069	−9.162
	M.C.O.[c]	−9.407	−9.373	−9.398	−9.353	−9.468
	EH[d]	−9.587	−9.506	−9.481	−9.489	−9.493
Pd	C.O	−8.652	−8.530	−8.498	−8.505	−8.478
	M.C.O.	−8.777	−8.815	−8.768	−8.736	−8.710
	EH	−8.934	−8.899	−8.876	−8.882	−8.833
Pt	C.O	−9.325	−9.209	−9.293	−9.168	−9.268
	M.C.O.	−9.674	−9.669	−9.618	−9.592	−9.693
	EH	−9.880	−9.796	−9.761	−9.724	−9.748

[a] The size of each cluster is 3×5×3 (23), 5×5×3 (38), 7×5×3 (53), 9×5×3 (68), and 5×5×5 (63). HOMO levels obtained by [b] cluster orbital, [c] modified cluster orbital, and [d] EH methods.

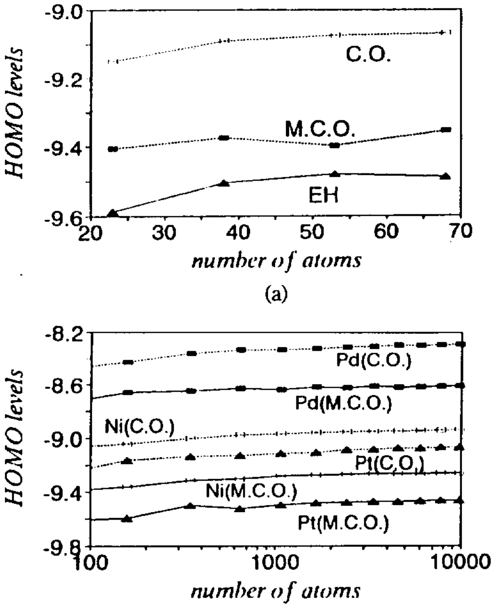
Table 4. Comparison of the Unit Electronic Energies[a] (in eV) of Various Metal Clusters Obtained by the Three Methods

Metal	Method	Number of atoms of each metal cluster				
		23	38	53	68	63
Ni	C.O.	−107.25	−107.77	−107.99	−108.11	−108.33
	M.C.O.	−102.50	−102.61	−102.66	−102.69	−102.71
	EH	−102.38	−102.47	−102.51	−102.53	−102.56
Pd	C.O.	−97.45	−97.81	−97.96	−98.04	−97.66
	M.C.O.	−94.69	−94.76	−94.78	−94.80	−94.80
	EH	−94.53	−94.57	−94.59	−94.60	−94.62
Pt	C.O.	−112.19	−112.84	−113.05	−113.17	−113.37
	M.C.O.	−107.99	−108.14	−108.20	−108.23	−108.28
	EH	−107.94	−108.08	−108.13	−108.15	−108.19

[a] Unit electronic energy is defined as the total electronic energy divided by the number of atoms of the cluster.

As a preliminary step to explicitly treat the off-diagonal submatrices, the overlap integrals are included and the results show much improvement, though there still remains the problem of the mixing of the cluster orbitals with different state indices. This is not so simple a problem, but the problem will be solved gradually by later studies.

Before closing the discussion, the convergency of physical properties with cluster size is briefly mentioned. The HOMO levels and the unit electronic energies of large Ni, Pd, and Pt clusters, obtained by the C.O. and M.C.O. methods (They can not, of course, be calculated by EH method.), are given in Table 5 and 6 with increasing size (less than ten thousand atoms). The changes of the HOMO levels are shown in Figure 3(b). Though the value to which each physical property



(a)

(b)

Figure 3. (a) Comparison of the HOMO levels (in eV) of four nickel clusters obtained by cluster orbital (dotted line with empty squares), modified cluster orbital (dotted line with filled squares), and EH (solid line with filled triangles) methods. It is shown that the HOMO levels obtained by the M.C.O. method is much closer to the results of EH calculation. (b) The change of the HOMO levels (in eV) of Ni (empty squares), Pd (filled squares), and Pt (filled triangles) clusters of various size calculated by C.O. (dotted lines) and M.C.O. (solid lines) methods. The number of the atoms are given in abscissa in logarithmic scale. The HOMO levels calculated by the M.C.O. method are lower than those by the C.O. method and it is shown that the HOMO levels do not change much as the cluster size increases.

Table 5. Change of the HOMO Levels (in eV) of Ni, Pd, and Pt Clusters with Increasing Size Obtained by C.O. and M.C.O. Methods

N_A	N_B	N_C	Number of metal atoms[a]	Ni		Pd		Pt	
				C.O.	M.C.O.	C.O.	M.C.O.	C.O.	M.C.O.
7	5	3	53	−9.074	−9.398	−8.498	−8.768	−9.293	−9.618
9	7	5	158	−9.045	−9.361	−8.428	−8.662	−9.164	−9.595
11	9	7	347	−9.004	−9.313	−8.362	−8.652	−9.134	−9.502
13	11	9	644	−8.981	−9.302	−8.338	−8.631	−9.127	−9.525
15	13	11	1,073	−8.968	−9.282	−8.335	−8.642	−9.115	−9.496
17	15	13	1,658	−8.958	−9.273	−8.322	−8.622	−9.109	−9.484
19	17	15	2,423	−8.957	−9.266	−8.315	−8.623	−9.089	−9.479
21	19	17	3,392	−8.954	−9.259	−8.308	−8.614	−9.086	−9.473
23	21	19	4,589	−8.950	−9.262	−8.298	−8.620	−9.076	−9.473
25	23	21	6,038	−8.945	−9.259	−8.296	−8.617	−9.075	−9.466
27	25	23	7,763	−8.941	−9.257	−8.294	−8.614	−9.069	−9.465
29	27	25	9,788	−8.939	−9.258	−8.291	−8.611	−9.067	−9.462

[a] The number of metal atoms is $(N_A N_B N_C + 1)/2$.

Table 6. Change of the Unit Eletronic Energies (in eV) of Ni, Pd, and Pt Clusters with Increasing Size Obtained by C.O and M.C.O. Methods

Number of metal atoms	Ni		Pd		Pt	
	C.O.	M.C.O.	C.O.	M.C.O.	C.O.	M.C.O.
53	−107.99	−102.66	−97.96	−94.78	−113.05	−108.20
158	−108.92	−102.82	−98.55	−94.87	−113.98	−108.43
347	−109.35	−102.89	−98.82	−94.91	−114.43	−108.53
644	−109.63	−102.94	−98.98	−94.94	−114.71	−108.59
1,073	−109.82	−102.97	−99.09	−94.96	−114.91	−108.62
1,658	−109.96	−102.99	−99.17	−94.97	−115.05	−108.65
2,423	−110.06	−103.00	−99.23	−94.98	−115.16	−108.67
3,392	−110.15	−103.02	−99.28	−94.99	−115.24	−108.69
4,589	−110.21	−103.03	−99.32	−95.00	−115.31	−108.70
6,038	−110.27	−103.04	−99.35	−95.00	−115.36	−108.71
7,763	−110.31	−103.04	−99.37	−95.01	−115.41	−108.72
9,788	−110.35	−103.05	−99.40	−95.01	−115.45	−108.73

converges may not be specified, a fact is evident that the HOMO levels and the unit electronic energies converge, or at least make a less change, with the cluster size. This fact is useful to verify the validity of the cluster approach to find the bulk properties of solids. They also make it possible to study the chemisorption by use of this method—our next work. The works on the convergency of the cluster model for the study of chemisorption have sometimes been performed,[11,12] but they were restricted to very small clusters. Minot *et al.*[13] attacked this problem with the analytical expression of the model, but the work was restricted to the one-atomic-orbital case. Now that it has been verified that the modified cluster orbital method may reproduce the results of the EH calculation, at least concerning to the physical properties related to the energy levels, the next step is to reveal whether the physical properties related to the wave functions, say Mulliken atomic population,[14] may also do so or not. If the results are satisfactory, the method will be really applied to the chemisorption problem on metal surfaces.

Conclusion

The energy levels obtained by the modified cluster orbital method agree very well with those by the EH calculation for one-atomic-orbital case (H clusters). If nine atomic orbitals, instead of one atomic orbital, are allowed per site (metal cluster), a little inconsistency arises because of the assumption that the modified cluster orbitals with different state indices do not mix together; nevertheless the results (the physical properties related to the energy levels) show much improvement compared with those calculated by the previous method, especially quantitatively. The analytic methods (this and the previous[1,2] works) have an advantage that the limitation on the cluster size is eliminated at the cost of the approximations given, so they are very useful for treating large clusters (clusters with more than a hundred or so atoms) whose solutions cannot be found by any other method of quantum chemistry. Studies from now on will be concentrated on the chemisorption problem with the modified cluster orbital method, after revealing that the wave functions obtained by this method are also in accordance with those found by the EH calculation.

From the earlier work[1] on the analytic solutions of an f.c.c. metal cluster, it has been assumed that the cluster belong to the point group D_{2h}. Much simplification in a submatrix of nine by nine (a diagonal submatrix) has been made from the symmetry condition. The symmetry, however, may be broken by loosening the restriction on N_A, N_B, and N_C and a new result may be obtained in this case. This symmetry breaking may be one of the efforts to deal with the off-diagonal submatrices (The summation rules[1], then, will change.). Or, the parameters $-E_{z^2,z^2}(110), S_{z^2,z^2}(200),\cdots-$ may be replaced by other ones. In these ways, the efforts to treat the off-diagonal submatrices more explicitly will also be continued.

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Encapsulation Characteristics of Gas Molecules in the Cavities of Zeolite A

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Encapsulation capacities (V_{gas}) of, H_2, N_2, CO, CH_4 and CO_2 for $Cs_{2.5}Na_{9.5}$-A (Cs-A) and Na_{12}-A (Na-A) zeolites have been measured in order to understand the effect of molecular properties on the V_{gas}. With appropriate number of large blocking cations on the main windows of cavities in zeolite A, gas molecules can be encapsulated in both the α- and β-cages, resulting in much large V_{gas}. V_{gas} is proportional to the encapsulation pressure (P_e) and is also dependent on the molecular properties of encapsulated gases themselves, especially on intermolecular forces originated from the quadrupole moments of molecules in the molecular-dimensioned cavities of zeolite A. At the low range of P_e, molecules with larger V_{gas} and intermolecular forces apparently have smaller increasing tendencies of V_{gas} upon increases in P_e, showing a linear relationship between the tendencies and intermolecular forces rather than their sizes. Interactions between encapsulated molecules of CH_4 and framework of Cs-A have been estimated and they seem to depend on the number of encapsulated molecules per unit cell. On the basis of calculated density of CO_2, presence of liquid-like phase for the encapsulated molecules in the molecular dimensioned cavities of zeolite A is postulated.

Introduction

For the purposes of storage and transport, gas molecules with kinetic diameters (σ)[1] slightly larger than the diameter of zeolitic windows can be enforced into the molecular-dimensioned cavities of zeolite by heating zeolite with pressured gases around and they can be entrapped by rapid quenching to ambient conditions (encapsulation).[2,3] Unlike chemi- or physisorbed gas molecules, the encapsulated gas molecules in the zeolitic cavities can sustain high pressure without leakage even at room temperature and they can be controllably released by the relaxation of window blocking such as by reheating the zeolite or by exposing the zeolite to small polar molecules (decapsulation).[4-9]

The entrance of gas molecules into the openings at the surface of microcrystals of the zeolites can be controlled by relative sizes of gas molecules and zeolitic windows modified by pore-size engineering.[5,10-14] En- and decapsulation of molecules in the zeolitic cavities can then be performed by invoking vigorous thermal vibrations of zeolite framework in