

Analytic Solutions of Finite F.C.C. Metal Clusters with Cluster Orbitals

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By use of cluster orbitals, analytic solutions of finite face-centered cubic clusters are obtained. Taking interactions between up to the second nearest neighbors into account, the forms of all the elements of the Hamiltonian matrix are found explicitly within Hückel approximation. By adopting D_{2h} point group to the cluster, the matrix is simplified. We assume that the cluster orbitals can mix together only when their state indices are identical. It is then possible to calculate various physical properties of face-centered cubic metal clusters and example are shown for palladium clusters. The results show that density of states and projected density of states are similar, qualitatively, with those obtained by extended Hückel calculation.

Introduction

There have been some efforts to find analytic solutions (energies and wave functions) of finite metal clusters.¹⁻⁶ These analytic methods have an advantage that the limitation on the size of a cluster is eliminated, so they are very useful for treating large clusters whose solutions cannot be obtained by other methods. Messmer¹ obtained analytic solutions of simple cubic (s.c.) metal clusters, taking interactions between only the nearest neighbors into account, within Hückel scheme. He allowed only atomic s orbital on each atom. Bilek and Kadura² obtained expressions for energies and wave functions of face-centered cubic (f.c.c.) clusters. They recognized an s.c. cluster as two interpenetrated f.c.c. clusters and treated interactions between only the nearest neighbors allowing only s orbital per site.

Even if atomic orbitals other than s are allowed per site, analytic solutions can be obtained as long as one type of orbitals are allowed. We solved this problem for s.c., f.c.c., and b.c.c. (body-centered cubic) clusters.³ We obtained solutions by considering interactions between up to the fourth nearest neighbors for s.c. (these correspond to the second nearest neighbors for f.c.c. and b.c.c.). Another approach is that of Salem⁴⁻⁶, who discussed the mixing of cluster orbitals of one s -type and of five d -types by taking interactions between only the nearest neighbors into account.

In the present work, we treat f.c.c. metal clusters and examine mixing of nine types of cluster orbitals – one s -type, three p -types, and five d -types – within Hückel scheme including interactions between up to the second nearest (the fourth in case of s.c.) neighbors. First of all, the Hamiltonian matrix is simplified by adopting point group D_{2h} to the cluster. With Hückel approximation we can find all the elements of the Hamiltonian matrix explicitly. This means that it is possible to know how the interactions between any pairs of cluster orbitals are expressed. By diagonalizing this Hamiltonian matrix numerically, energies and wave functions of the cluster can be obtained. However, our goal is not to perform this calculation, but to obtain analytic solutions of the cluster. For this purpose, we assume that cluster orbitals can mix together only if the state indices of them are identi-

cal. This assumption is based on the forms of the analytic solutions for infinite crystals obtained by Slater and Koster⁷. From this assumption, we can make much simplification and final (numerical) calculation is made easy. We obtain density of states (DOS) and projected density of states (PDOS) of d orbitals (DOS projected on d -types of cluster orbitals; it is equivalent to DOS projected on atomic d orbitals, if atomic orbitals are used as a basis) of f.c.c. palladium (Pd) clusters using our scheme. The results are compared with those obtained by extended Hückel (EH) calculation, which show qualitative similarities. However, a flaw is that the mixings of cluster orbitals are not included fully, that is, off-diagonal submatrices are neglected in calculation.

D_{2h} Cluster

We define a cluster orbital of ϕ -type (ϕ is one of the nine atomic orbitals – s , x , y , z , $x^2 - y^2$, z^2 , xy , xz , and yz ; note, for instance, that x denotes atomic p_x orbital) of a finite f.c.c. metal cluster with rectangular parallelepiped shape, whose master (simple) cubic cluster has N_A , N_B , and N_C atoms along x -, y -, and z -axes, as follows:³

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

where N_0 is the normalization constant

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

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 , respectively, and they must satisfy the condition³ $\xi + \eta + \zeta \leq 3\pi/2$. This means that the number of cluster orbitals of ϕ -type equals to the number of atoms of the f.c.c. cluster. We call (l, m, n) a state index. The indices i, j , and k of the summation run from 1 to N_A , N_B , and N_C , respectively, and they label the atom. The asterisk(*) of the summation denotes the restriction of $i + j + k = \text{odd}$, for atoms lie only

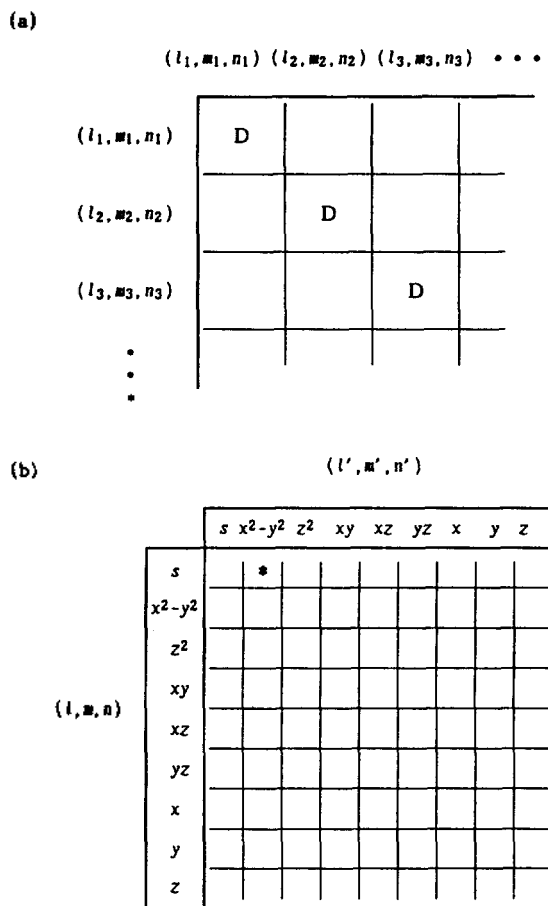


Figure 1. (a) The form of Hamiltonian matrix composed of elements denoting interactions between cluster orbitals. Blocks marked with "D" are diagonal submatrices and the others off-diagonal submatrices. Each block is made up of $81(9 \times 9)$ elements. (b) The form of one of the blocks of (a) representing interactions between nine cluster orbitals with a state index (l, m, n) and those with (l', m', n') . Each square corresponds to an element of this submatrix. For example, the element marked with "*" is $\langle \psi_l^{m'n} | H^{l'l'} | \psi_{l'}^{m'n} \rangle$.

on these sites in case of an f.c.c. cluster (With the same reason, there is no loss of generality if we assume that $i+j+k = \text{even}$).

Now from these cluster orbitals we can set up Hamiltonian matrix (Figure 1) composed of submatrices which denote interactions between nine cluster orbitals with a state index (l, m, n) and those with (l', m', n') . So, our task is to diagonalize this Hamiltonian matrix and to obtain the eigenvalues (energies) and eigenvectors (wave functions) of the cluster. Of course, the elements of the matrix should be known first. Before doing this, however, we allow the cluster to belong to a point group and from the symmetry conditions we will simplify the elements of the matrix, *i.e.*, make many elements vanish.

We assume that N_A , N_B , and N_C are all odd integers, and that they are distinct. Then we can assign the point group D_{2h} to this f.c.c. cluster. (If N_A , N_B , and N_C are all odd, each axis - x , y , and z -axes - is C_2 -axis and much simplification can be made from the symmetry conditions of each cluster

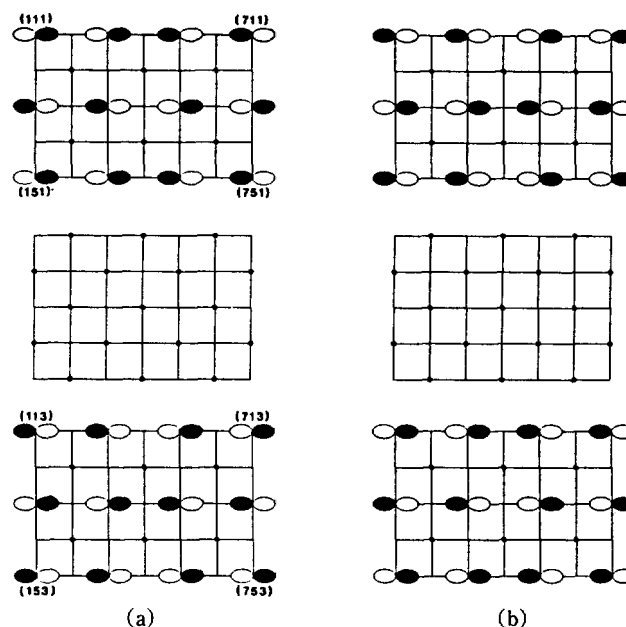


Figure 2. Schematic diagrams for finding the characters of ψ_r^{232} with $(N_A, N_B, N_C) = (7, 5, 3)$ under eight symmetry operations of point group D_{2h} . (a) Form of this cluster orbital, $N_0 \sum_{i,j,k} p_x(i, j, k) \left[\sin \frac{i\pi}{4} \sin \frac{j\pi}{2} \sin \frac{k\pi}{2} \right]$. The upper figure corresponds to the upper layer ($k=1$) of the cluster, the middle figure the middle layer ($k=2$), and the bottom figure the bottom layer ($k=3$). Since this cluster orbital is a linear combination of atomic orbitals, the coefficients of atomic orbitals may be zero, and these atoms are indicated by dots. By eight symmetry operations this orbital can be either unchanged (for E , $C_2(z)$, $\sigma(xz)$, and $\sigma(yz)$) or change all the signs of each lobe (for the others) as (b). The characters are +1 or -1 for (a) and (b), respectively.

orbital. Besides, if the point group is D_{4h} ($N_A = N_B \neq N_C$) or O_h ($N_A = N_B = N_C$), many degeneracies which may blur the general feature of the matrix can arise.)

Now, we can find the irreducible representation to which each cluster orbital belongs, from the characters of each cluster orbital under eight symmetry operations of point group D_{2h} . Figure 2, for example, shows schematic diagrams for how to obtain the characters of ψ_r^{232} with $(N_A, N_B, N_C) = (7, 5, 3)$ under eight symmetry operations of point group D_{2h} . This cluster orbital is a linear combination of atomic p_x orbitals and the form is given in Figure 2(a). By four symmetry operations [$C_2(x)$, $C_2(y)$, i , and $\sigma(xy)$], the cluster orbital is changed to the form shown in Figure 2(b), and it is unchanged by the other four operations of the group. So the characters are +1 for E , $C_2(z)$, $\sigma(xz)$, and $\sigma(yz)$, and -1 for $C_2(x)$, $C_2(y)$, i , and $\sigma(xy)$. Generally, with some algebraic manipulations (for detailed derivations, see Appendices 1) one can find that, for a given state index (l, m, n) , the character of a cluster orbital under a certain symmetry operation can be expressed as a product of two factors, one of which results from the change of the signs of atomic orbitals comprising the cluster orbital, the other from the conditions of the parities of the state index. Table 1 shows these two factors of each type of cluster orbital under each symmetry

Table 1. Two Factors Comprising the Characters of Each Type of Cluster Orbitals under Each Symmetry Operation

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
s	+	+	+	+	+	+	+	+
p_x	+	-	-	+	-	+	+	-
p_y	+	-	+	-	-	+	-	+
p_z	+	+	-	-	-	-	+	+
$d_{x^2-y^2}$	+	+	+	+	+	+	+	+
d_z^2	+	+	+	+	+	+	+	+
d_{xy}	+	+	-	-	+	+	-	-
d_{xz}	+	-	+	-	+	-	+	-
d_{yz}	+	-	-	+	+	-	-	+
Factors ^a	2	$l+m$	$l+n$	$m+n$	$\frac{l+m}{+n+1}$	$n+1$	$m+1$	$l+1$

^aFactors are the exponents with the base -1, i.e., if the factor is $l+m$, then this means $(-1)^{l+m}$. Products of this factor and the sign of each row of the column to which factor belongs are the characters.

Table 2. The Irreducible Representations to Which Cluster Orbitals Belong According to Their Parities

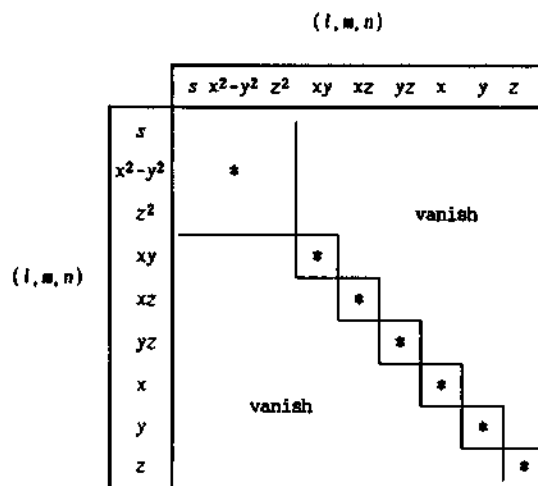
D_{2h}	eee	eeo^a	oeo	ooo	oee	oeo	oeo	ooo
s	A_g^b	B_{1g}	B_{2g}	B_{3g}	B_{3g}	B_{2g}	B_{1g}	A_g
p_x	B_{3g}	B_{2g}	B_{1g}	A_g	A_g	B_{1g}	B_{2g}	B_{3g}
p_y	B_{2g}	B_{3g}	A_g	B_{1g}	B_{1g}	A_g	B_{3g}	B_{2g}
p_z	B_{1g}	A_g	B_{3g}	B_{2g}	B_{2g}	B_{3g}	A_g	B_{1g}
$d_{x^2-y^2}$	A_g	B_{1g}	B_{2g}	B_{3g}	B_{3g}	B_{2g}	B_{1g}	A_g
d_z^2	A_g	B_{1g}	B_{2g}	B_{3g}	B_{3g}	B_{2g}	B_{1g}	A_g
d_{xy}	B_{1g}	A_g	B_{3g}	B_{2g}	B_{2g}	B_{3g}	A_g	B_{1g}
d_{xz}	B_{2g}	B_{3g}	A_g	B_{1g}	B_{1g}	A_g	B_{3g}	B_{2g}
d_{yz}	B_{3g}	B_{2g}	B_{1g}	A_g	A_g	B_{1g}	B_{2g}	B_{3g}

^aeeo means that l is even, m is even, and n is odd. ^bNote that ψ_s , $\psi_{x^2-y^2}$, and ψ_{z^2} belong to the same irreducible representations if their parities are same, i.e., if they lie in the same column.

operation. The characters of each cluster orbital depend on the conditions of the parities of the state index of them. The parity of a whole number is what makes us know whether the number is even or odd. Since each state index is composed of three whole numbers, there can be eight types of parities, say $l=even$, $m=even$, and $n=odd$. From this table, one finds that cluster orbitals with some parities belong to one of the eight irreducible representations of point group D_{2h} . These representations are given Table 2.

Diagonal Elements

From the facts that each cluster orbital belongs to one of the eight irreducible representations of point group D_{2h} , and that the cluster orbitals belonging to different irreducible representations do not mix together,⁸ Hamiltonian matrix can be simplified, i.e., many terms vanish due to the symmetry conditions. We set up Hamiltonian matrix composed of 9×9 submatrices which denote the mixings between nine cluster

**Figure 3.** The form of diagonal submatrices marked with "D" in Figure 1(a). Only elements (and a block) marked with "*" do not vanish by symmetry conditions of the cluster.

orbitals (say ψ_s , $\psi_{x^2-y^2}$, ψ_{z^2} , ..., etc.) with (l, m, n) and those with (l', m', n') . The size of this Hamiltonian matrix is $9N \times 9N$ where N is the number of metal atoms in the cluster. First, we will examine the mixing of cluster orbitals which have the same (l, m, n) 's. We call those submatrices "diagonal submatrices" of the full matrix.

Diagonal submatrices are composed of elements representing interactions between cluster orbitals whose state indices are identical, so their parities are necessarily identical. This means that they lie in the same column of Table 2. The table tells that only three cluster orbitals (ψ_s , $\psi_{x^2-y^2}$, and ψ_{z^2}) belong to the same irreducible representation and that the representations the others belong to are different from each other. Therefore, only these three cluster orbitals can mix together and other mixings do not occur. Figure 3 shows the form of this diagonal submatrix.

It is possible to calculate each element of the diagonal submatrices within Hückel approximation including interactions between up to the second nearest neighbors. (z^2/z^2), for example, can be calculated as follows:

$$\begin{aligned} \langle z^2/z^2 \rangle &\equiv \langle \psi_{z^2}^{lmn} | H^{eff} | \psi_{z^2}^{lmn} \rangle \\ &= N_o^2 \sum_{i,j,k} (\sin^2 i \xi \sin^2 j \eta \sin^2 k \zeta) \langle z^2(i, j, k) | H^{eff} | z^2(i, j, k) \rangle \\ &\quad + N.N. + S.N., \\ &= E_{z^2, z^2}(000) + N.N. + S.N., \end{aligned} \quad (4)$$

where $E_{z^2, z^2}(000)$ denotes the Coulomb integral of atomic d_z^2 orbital, i.e.,

$$E_{z^2, z^2}(000) \equiv \langle d_z^2(i, j, k) | H^{eff} | d_z^2(i, j, k) \rangle. \quad (5)$$

In Eq. (4) and from now on, the terms representing interactions between the nearest neighbors, and those representing interactions between the second nearest neighbors are shortened to $N.N.$ and $S.N.$, respectively. $N.N.$ and $S.N.$ can be calculated with some algebra (see Appendices 2 and 3) as follows:

$$N.N. = 4E_{z^2, z^2}(110) \cos \xi \cos \eta + 4E_{z^2, z^2}(011) \cos \eta \cos \zeta$$

Table 3. Elements of Diagonal Submatrices for a Given State Index

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

$$(x^2 - y^2/x^2 - y^2) = E_{x^2-y^2}(000) + 4 E_{x^2-y^2}(110) \cos\xi \cos\eta + 4 E_{x^2-y^2}(011) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{x^2-y^2}(200) [\cos 2\xi + \cos 2\eta] + 2 E_{x^2-y^2}(002) \cos 2\zeta + 4 E_{x^2-y^2}(200) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} \right] + 4 E_{x^2-y^2}(002) \frac{\sin^2\zeta}{N_C+1}$$

$$(z^2/z^2) = E_{z^2}(000) + 4 E_{z^2}(110) \cos\xi \cos\eta + 4 E_{z^2}(011) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{z^2}(200) [\cos 2\xi + \cos 2\eta] + 2 E_{z^2}(002) \cos 2\zeta + 4 E_{z^2}(200) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} \right] + 4 E_{z^2}(002) \frac{\sin^2\zeta}{N_C+1}$$

$$(xy/xy) = E_{xy}(000) + 4 E_{xy}(110) \cos\xi \cos\eta + 4 E_{xy}(011) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{xy}(200) [\cos 2\xi + \cos 2\eta] + 2 E_{xy}(002) \cos 2\zeta + 4 E_{xy}(200) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} \right] + 4 E_{xy}(002) \frac{\sin^2\zeta}{N_C+1}$$

$$(xz/xz) = E_{xz}(000) + 4 E_{xz}(110) \cos\xi \cos\zeta + 4 E_{xz}(011) [\cos\xi \cos\eta + \cos\eta \cos\zeta] + 2 E_{xz}(200) [\cos 2\xi + \cos 2\zeta] + 2 E_{xz}(002) \cos 2\eta + 4 E_{xz}(200) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\zeta}{N_C+1} \right] + 4 E_{xz}(002) \frac{\sin^2\eta}{N_B+1}$$

$$(yz/yz) = E_{yz}(000) + 4 E_{yz}(110) \cos\eta \cos\zeta + 4 E_{yz}(011) [\cos\xi \cos\eta + \cos\xi \cos\zeta] + 2 E_{yz}(200) [\cos 2\eta + \cos 2\zeta] + 2 E_{yz}(002) \cos 2\xi + 4 E_{yz}(200) \left[\frac{\sin^2\eta}{N_B+1} + \frac{\sin^2\zeta}{N_C+1} \right] + 4 E_{yz}(002) \frac{\sin^2\xi}{N_A+1}$$

$$(x/x) = E_{x,x}(000) + 4 E_{x,x}(110) [\cos\xi \cos\eta + \cos\xi \cos\zeta] + 4 E_{x,x}(011) \cos\eta \cos\zeta + 2 E_{x,x}(200) \cos 2\xi + 2 E_{x,x}(002) [\cos 2\eta + \cos 2\zeta] + 4 E_{x,x}(200) \frac{\sin^2\xi}{N_A+1} + 4 E_{x,x}(002) \left[\frac{\sin^2\eta}{N_B+1} + \frac{\sin^2\zeta}{N_C+1} \right]$$

$$(y/y) = E_{y,y}(000) + 4 E_{y,y}(110) [\cos\xi \cos\eta + \cos\eta \cos\zeta] + 4 E_{y,y}(011) \cos\xi \cos\zeta + 2 E_{y,y}(200) \cos 2\eta + 2 E_{y,y}(002) [\cos 2\xi + \cos 2\zeta] + 4 E_{y,y}(200) \frac{\sin^2\eta}{N_B+1} + 4 E_{y,y}(002) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\zeta}{N_C+1} \right]$$

$$(z/z) = E_{z,z}(000) + 4 E_{z,z}(110) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 4 E_{z,z}(011) \cos\xi \cos\eta + 2 E_{z,z}(200) \cos 2\zeta + 2 E_{z,z}(002) [\cos 2\xi + \cos 2\eta] + 4 E_{z,z}(200) \frac{\sin^2\zeta}{N_C+1} + 4 E_{z,z}(002) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} \right]$$

$$(s/x^2 - y^2) = (x^2 - y^2/s) = 4 E_{x^2-y^2}(011) [-\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{x^2-y^2}(200) [\cos 2\xi - \cos 2\eta] + 4 E_{x^2-y^2}(200) \left[\frac{\sin^2\xi}{N_A+1} - \frac{\sin^2\eta}{N_B+1} \right]$$

$$(s/z^2)^b = (z^2/s) = 4 E_{z^2}(110) \cos\xi \cos\eta + 4 E_{z^2}(011) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{z^2}(200) [\cos 2\xi + \cos 2\eta] + 2 E_{z^2}(002) \cos 2\zeta + 4 E_{z^2}(200) \left[\frac{\sin^2\xi}{N_A+1} + \frac{\sin^2\eta}{N_B+1} \right] + 4 E_{z^2}(002) \frac{\sin^2\zeta}{N_C+1}$$

$$(x^2 - y^2/z^2) = (z^2/x^2 - y^2) = 4 E_{x^2-y^2}(011) [-\cos\xi \cos\zeta + \cos\eta \cos\zeta] + 2 E_{x^2-y^2}(200) [\cos 2\xi - \cos 2\eta] + 4 E_{x^2-y^2}(200) \left[\frac{\sin^2\xi}{N_A+1} - \frac{\sin^2\eta}{N_B+1} \right]$$

^aξ, η, and ζ are defined by ξ ≡ $\frac{l\pi}{N_A+1}$, η ≡ $\frac{m\pi}{N_B+1}$, and ζ ≡ $\frac{n\pi}{N_C+1}$. See Eq. (3) of text. ^b(s/z²) ≡ <ψ_{i^{mn}}^l|H^{eff}|ψ_{j^{mn}}^l>. ^cE_{x,z}²(110) ≡ <s(i, j, k)|H^{eff}|d_z²(i+1, j+1, k)>.

$$+ 4E_{z^2}(101) \cos\xi \cos\zeta \tag{6a} \qquad + 2E_{z^2}(002) \cos 2\zeta + 4E_{z^2}(002) \frac{\sin^2\zeta}{N_C+1}, \tag{6b}$$

and $S.N. = 2E_{z^2}(200) \cos 2\xi + 4E_{z^2}(200) \frac{\sin^2\xi}{N_A+1}$ where $E_{z^2}(110) = \langle d_z^2(i, j, k) | H^{eff} | d_z^2(i+1, j+1, k) \rangle$ (7a)

$$+ 2E_{z^2}(020) \cos 2\eta + 4E_{z^2}(020) \frac{\sin^2\eta}{N_B+1}$$

and $E_{z^2}(200) = \langle d_z^2(i, j, k) | H^{eff} | d_z^2(i+2, j, k) \rangle.$ (7b)

Since $E_{z^2, z}(011) = E_{z^2, z}(101)$ and $E_{z^2, z}(200) = E_{z^2, z}(020)$, (z^2/z^2) can be written in more compact form as

$$\begin{aligned} (z^2/z^2) = & E_{z^2, z}(000) + 4E_{z^2, z}(110) \cos\xi \cos\eta \\ & + 4E_{z^2, z}(011) [\cos\xi \cos\zeta + \cos\eta \cos\zeta] \\ & + 2E_{z^2, z}(200) [\cos 2\xi + \cos 2\eta] + 2E_{z^2, z}(002) \cos 2\zeta \\ & + 4E_{z^2, z}(200) \left[\frac{\sin^2\xi}{N_A + 1} + \frac{\sin^2\eta}{N_B + 1} \right] + 4E_{z^2, z}(002) \frac{\sin^2\zeta}{N_C + 1}. \end{aligned} \quad (8)$$

The other elements can be calculated similarly and they are shown in Table 3. The terms including $(N_A + 1)^{-1}$, $(N_B + 1)^{-1}$, and $(N_C + 1)^{-1}$ arise from the surface atoms and they vanish as N_A , N_B , and N_C go to infinity, *i.e.*, as the size of the cluster increases infinitely.

The elements of the off-diagonal submatrices (interactions between cluster orbitals with different state indices) can be found with similar method. However, their forms are not so simple as the diagonal ones. We will discuss these in next section. We will see that they also contain energy parameters, say $E_{z^2, z}(110)$, as the elements of the diagonal submatrices. These energy parameters may be obtained from the extended Hückel (EH) calculation. So, it is possible to obtain numerical values of all the elements of the Hamiltonian matrix. By numerical diagonalization method, one can find energies and wave functions of the cluster. However, in practice, this numerical diagonalization is restricted by the size of the matrix.

Our goal is not to diagonalize this Hamiltonian matrix numerically, but to obtain analytic solutions of the cluster. Even if the values of all the elements are known analytically, it is very difficult – nearly impossible – to diagonalize this matrix analytically. So, one needs some approximations to find eigenvalues (and eigenvectors) of the cluster. In case of infinite crystals, a wave vector \mathbf{k} is defined and this is a “good” quantum number, so Bloch sums with different wave vectors do not mix with each other. Bloch sums are the counterparts of the cluster orbitals. Similarly the wave vectors are the counterparts of the state indices. So we may reasonably expect that the terms representing the mixing between cluster orbitals with different state indices will vanish as the size of the cluster increases. Keeping this in mind, we assume that mixing between cluster orbitals with different state indices do not occur in all cases. This means that elements obtained in this section are only nonvanishing elements, that is, the Hamiltonian matrix is composed of only N diagonal blocks, whose size is 9×9 . Now our task is to diagonalize these 9×9 submatrices for N times. These diagonalizations are performed numerically. In fact, each of these submatrices is also decomposed into a 3×3 block and 6 diagonal elements. So only diagonalizations (N times) of these 3×3 blocks are needed (Figure 3). Even if the size of the cluster (the number of metal atoms in the cluster) increases, there is no problem, for only the number of calculations of these diagonalizations increases.

We carry out these calculations, on the assumption given above, for palladium clusters. The energy parameters are obtained from EH calculations done previously in our lab.⁹ Figure 4 shows density of states (DOS) and projected DOS (PDOS) of d orbitals (shaded areas) of Pd clusters. The clus-

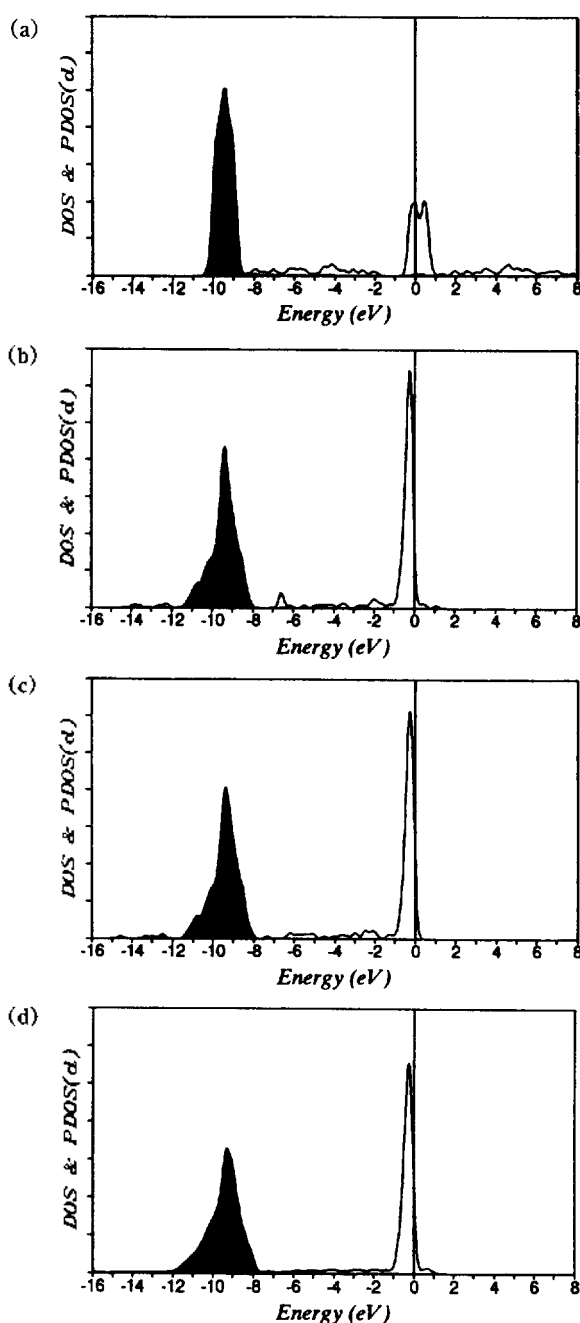


Figure 4. Curves denoting DOS and PDOS of d orbitals (shaded areas) of Pd_{53} and Pd_{1073} clusters. (a) DOS and PDOS of Pd_{53} cluster by EH calculation, (b) by our method taking interactions between only the nearest neighbors into account, (c) up to the second nearest neighbors, and (d) for Pd_{1073} cluster with our method up to the second nearest neighbors. Note that the scale of ordinate is arbitrary. Calculated HOMO levels are (a) -8.84 , (b) -8.53 , (c) -8.50 , and (d) -8.34 eV.

ters used for calculations are Pd_{53} for (a)-(c), and Pd_{1073} for (d). In case of Pd_{53} cluster, two methods are used for calculations, one [Figure 4(a)] is EH and the other [Figure 4(b) and (c)] is our scheme. Curves shown in Figure 4(b) is those of DOS and PDOS of Pd_{53} cluster when interactions between only the nearest neighbors are considered and (c) those up to the second nearest neighbors. From these, we can see

that the forms of the curves of DOS and PDOS by our method are similar, qualitatively, with those obtained by EH calculation. A sharp falls above 0 eV for (b) and (c) are thought to originate from the fact that we took only diagonal submatrices into account. In a diagonal submatrix, terms denoting interactions between p orbitals appear only on diagonal positions. This means that the mixings of p orbitals are not included fully. However, since HOMO of the cluster lies about $-8 \sim -9$ eV [HOMO levels are calculated as (a) -8.84 , (b) -8.53 , (c) -8.50 , and (d) -8.34 eV], these orbitals are not significant. From (b) and (c), we know that there are few problems if interactions between the second nearest neighbors are neglected. The matter will be mentioned in next section. Since our approach is analytic, the limitation on the size of the cluster is eliminated. As an example we carry out calculations for Pd_{1073} cluster. For this cluster, the size of the Hamiltonian matrix is $9,657 \times 9,657$ and direct numerical diagonalization of this matrix is second to impossible. However, we can do it, though approximately, and the results are shown in Figure 4(d).

In next section, the forms of the elements of off-diagonal submatrices excluded in this section will be discussed. We will see that the forms of any elements can be known explicitly. However, solving the full matrix analytically is impossible, so we will not include these off-diagonal elements in calculation.

Mixing of Cluster Orbitals with Different State Indices

We have shown that each cluster orbital with some parities belongs to one of the eight irreducible representations of point group D_{2h} (Table 2). By rearranging Table 2, cluster orbitals (with some parities) belonging to the same irreducible representations can be collected. These are given in Table 4. From the symmetry conditions, it follows that the cluster orbitals in the same row mix together and that those in different rows do not mix. A very careful examination of this table may lead to the fact that there are some rules on the parity conditions for cluster orbitals belonging to the same irreducible representation. Say, in all of the eight rows, only the parities of l are changed (*even* \rightarrow *odd*, *odd* \rightarrow *even*) if we move from the first column to the second one. This means that the cluster orbitals of s -type and those of x -type mix together only if their parities of l are different. Rules of this kind are seen in all pairs of columns. From these, one finds some rules on the parity conditions of the mixing of cluster orbitals. That is,

$$\langle \psi_s^{lmn} | H^{eff} | \psi_{s'}^{l'm'n'} \rangle \neq 0,$$

if the following parity conditions are satisfied: (i) the parities of l and l' should be different if x 's appear odd times in both ϕ and ϕ' (for instance, the number of x 's is three for (x^2-y^2/x) , and two for (x/x) , etc.); (ii) for y and z , same conditions hold on the parities of m and m' , and n and n' ; and (iii) the corresponding parities should be same when the numbers of occurrence of x , y , or z are even. These rules hold for the above example $-s$ and x .

How can we explain the above rules? For the simplicity of discussion, interactions between only the nearest neighbors are treated. (We showed that, for palladium, there is

Table 4. Parity Conditions for Each Type of Cluster Orbitals to Belong to the Same Irreducible Representations

D_{2h}	s	x	y	z	x^2-y^2	z^2	xy	xz	yz
A_g	ooo	oee	oee	oee	ooo	ooo	eeo	eeo	eeo
B_{1g}	eeo	oee	ooo	eee	eeo	eeo	ooo	oee	oee
B_{2g}	oee	oee	eee	ooo	oee	oee	oee	ooo	eeo
B_{3g}	oee	eee	oee	ooo	oee	oee	oee	eeo	ooo
A_u	eee	oee	oee	ooo	eee	eee	oee	oee	ooo
B_{1u}	oee	oee	ooo	ooo	oee	oee	eee	ooo	oee
B_{2u}	ooo	eee	ooo	eee	ooo	ooo	ooo	eee	oee
B_{3u}	ooo	ooo	eee	ooo	ooo	ooo	ooo	ooo	eee

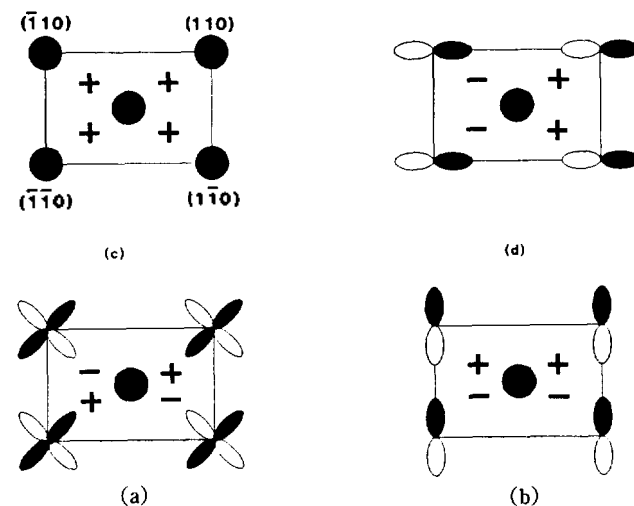


Figure 5. Four cases on the relative signs of the resonance integrals between an s orbital and (a) s , (b) p_x , (c) d_{yz} , (d) p_y orbitals, each pair being centered on the positions of the nearest neighbors. Note that the signs are not absolute ones, but relative ones by setting the sign of $E_{s,s}(110)$ positive.

not much difference when we neglect interactions between the second nearest neighbors.) If ϕ and ϕ' are same, four resonance integrals on a plane, say $E_{x,x}(110)$, $E_{x,x}(1\bar{1}0)$, $E_{x,x}(\bar{1}10)$, and $E_{x,x}(\bar{1}\bar{1}0)$, are identical. In general, however, this is not the case and four cases arise for resonance integrals, for example, on xy -plane (Figure 5). For these four cases, the terms denoting interactions between the nearest neighbors on xy -plane can be calculated. For (a),

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_s^{l'm'n'} \rangle \Big|_{\substack{xy\text{-plane} \\ \text{the nearest neighbors}}} \\ &= N_0^2 E_{s,s}(110) \sum_{i,j,k} (\sin i \zeta \sin j \eta \sin k \zeta) \{ [\sin(i+1)\zeta' \sin(j+1)\eta' \sin k \zeta'] \\ & \quad + [\sin(i+1)\zeta' \sin(j-1)\eta' \sin k \zeta'] + [\sin(i-1)\zeta' \sin(j+1)\eta' \\ & \quad \times \sin k \zeta'] + [\sin(i-1)\zeta' \sin(j-1)\eta' \sin k \zeta'] \} \\ &= N_0^2 E_{s,s}(110) \sum_{i,j,k} (\sin i \zeta \sin j \eta \sin k \zeta) \{ [\sin(i+1)\zeta' + \sin(i-1)\zeta'] \\ & \quad \times [\sin(j+1)\eta' + \sin(j-1)\eta'] \sin k \zeta' \} \\ &= 4N_0^2 E_{s,s}(110) \cos \zeta' \cos \eta' \\ & \quad \times \sum_{i,j,k} (\sin j \zeta \sin i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (9)$$

For (b),

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_x^{l'm'n'} \rangle \Big|_{\substack{xy\text{-plane} \\ \text{the nearest neighbors}}} \\ &= N_0^2 E_{s,x}(110) \sum_{i,j,k} (\sin i \zeta \sin j \eta \sin k \zeta) [\sin(i+1)\xi' - \sin(i-1)\xi'] \\ & \quad \times [\sin(j+1)\eta' + \sin(j-1)\eta'] \sin k \zeta' \\ &= 4N_0^2 E_{s,x}(110) \sin \xi' \cos \eta' \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \cos i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (10)$$

For (c) and (d),

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_{xy}^{l'm'n'} \rangle \Big|_{\substack{xy\text{-plane} \\ \text{the nearest neighbors}}} \\ &= 4N_0^2 E_{s,xy}(110) \sin \xi' \sin \eta' \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \cos i \zeta') (\sin j \eta \cos j \eta') (\sin k \zeta \sin k \zeta') \end{aligned} \quad (11)$$

and

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_y^{l'm'n'} \rangle \Big|_{\substack{xy\text{-plane} \\ \text{the nearest neighbors}}} \\ &= 4N_0^2 E_{s,y}(110) \cos \xi' \sin \eta' \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \sin i \zeta') (\sin j \eta \cos j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (12)$$

By extending these results to others (*yz* and *xz*) planes, we can obtain the terms denoting interactions between the nearest neighbors for the above four pairs of cluster orbitals as:

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_s^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 E_{s,s}(110) \cos \xi' \cos \eta' + E_{s,s}(011) \cos \eta' \cos \zeta' \\ & \quad + E_{s,s}(101) \cos \zeta' \cos \xi' \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \sin i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'), \end{aligned} \quad (13)$$

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_x^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 [E_{s,x}(110) \sin \xi' \cos \eta' + E_{s,x}(011) \cos \eta' \cos \zeta' \\ & \quad + E_{s,x}(101) \cos \zeta' \cos \xi'] \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \sin i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'), \end{aligned} \quad (14)$$

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_{xy}^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 [E_{s,xy}(110) \sin \xi' \sin \eta' + E_{s,xy}(011) \sin \eta' \cos \zeta' \\ & \quad + E_{s,xy}(101) \cos \zeta' \sin \xi'] \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \cos i \zeta') (\sin j \eta \cos j \eta') (\sin k \zeta \sin k \zeta'), \end{aligned} \quad (15)$$

and

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_y^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 [E_{s,y}(110) \cos \xi' \sin \eta' + E_{s,y}(011) \sin \eta' \cos \zeta' \\ & \quad + E_{s,y}(101) \cos \zeta' \cos \xi'] \end{aligned}$$

$$\times \sum_{i,j,k} (\sin i \zeta \sin i \zeta') (\sin j \eta \cos j \eta') (\sin k \zeta \sin k \zeta'). \quad (16)$$

Note that $E_{s,s}(110) = E_{s,s}(011) = E_{s,s}(101)$, so Eq. (13) can be rewritten as

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_s^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 E_{s,s}(110) [\cos \xi' \cos \eta' + \cos \eta' \cos \zeta' + \cos \zeta' \cos \xi'] \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \sin i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (17)$$

Besides, $E_{s,x}(110) = E_{s,x}(101)$ and $E_{s,x}(011)$ equals zero, so Eq. (14) can also be rewritten as

$$\begin{aligned} & \langle \psi_s^{lmn} | H^{eff} | \psi_x^{l'm'n'} \rangle \Big|_{\text{the nearest neighbors}} \\ &= 4N_0^2 E_{s,x}(110) \sin \xi' (\cos \eta' + \cos \zeta') \\ & \quad \times \sum_{i,j,k} (\sin i \zeta \cos i \zeta') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (18)$$

For final solutions, however, we must know the resonance integral values and they may be obtained from EH calculation. So, if we write Eqs. (17) and (18) as (13) and (14), there are no problems. And for systematic treatment, the forms of Eqs. (13)-(16) are preferred to those of Eqs. (17) and (18). From Eqs. (13)-(16), we can see that they are composed of two factors, one of which is a simple number and the other the value obtained by sum of some terms.

From Eqs. (13)-(16) and from the rules on the mixing of cluster orbitals (Table 4), one notices three facts, that is: (i) if the parities of *l* and *l'* (or those of *m* and *m'*, or *n* and *n'*) should be different for mixing, a factor $\sin i \zeta \cos i \zeta'$ (or $\sin j \eta \cos j \eta'$, or $\sin k \zeta \cos k \zeta'$) appears in the summations; (ii) factors associated with same parities are products of two sine functions, *i.e.*, a factor $\sin i \zeta \sin i \zeta'$ appears in the summation if *l* and *l'* should have same parities for mixing; and (iii) if $\sin i \zeta \sin i \zeta'$ factor appears in the summation, the constant factor contains $\cos \xi'$, if factor of $\sin i \zeta \cos i \zeta'$ appears, it contains $\sin \xi'$. These results can be extended to any pairs of cluster orbitals. Therefore, it is possible to write down all of the off-diagonal elements of the Hamiltonian matrix explicitly, that is

$$\begin{aligned} & \langle \psi_\phi^{lmn} | H^{eff} | \psi_\phi^{l'm'n'} \rangle = E_{\phi,\phi}(000) \delta_{\phi,\phi} \\ & \quad + 4N_0^2 [E_{\phi,\phi}(110) \left(\frac{\sin \xi'}{\cos \xi'} \right) \left(\frac{\sin \eta'}{\cos \eta'} \right) + E_{\phi,\phi}(011) \left(\frac{\sin \eta'}{\cos \eta'} \right) \left(\frac{\sin \zeta'}{\cos \zeta'} \right) \\ & \quad + E_{\phi,\phi}(101) \left(\frac{\sin \zeta'}{\cos \zeta'} \right) \left(\frac{\sin \xi'}{\cos \xi'} \right)] \left[\sum_{i,j,k} \sin i \zeta \left(\frac{\cos i \zeta'}{\sin i \zeta'} \right) \right. \\ & \quad \left. \times \sin j \eta \left(\frac{\cos j \eta'}{\sin j \eta'} \right) \sin k \zeta \left(\frac{\cos k \zeta'}{\sin k \zeta'} \right) \right]. \end{aligned} \quad (19)$$

If the parities of *l* and *l'* should be different for mixing of given two cluster orbitals, upper factors including ξ' (and those including η' for *m* and *m'*, and ζ' for *n* and *n'*) are selected. Lower factors (ξ' , η' , or ζ' according to *l*, *m*, or *n*) are selected when the same parities are needed.

The problem is that the summation in Eq. (19) cannot be separated, for the restriction on the summation that $i+j+k = \text{odd}$. So, if we are to separate this summation, it must be decomposed into four summations as

$$\sum_{i,j,k} = \sum_{i, \text{even}} \sum_{j, \text{even}} \sum_{k, \text{odd}} + \sum_{i, \text{even}} \sum_{j, \text{odd}} \sum_{k, \text{even}} + \sum_{i, \text{odd}} \sum_{j, \text{even}} \sum_{k, \text{even}} + \sum_{i, \text{odd}} \sum_{j, \text{odd}} \sum_{k, \text{odd}} \quad (20)$$

Each of the summation in the right-hand side of Eq. (20) can be calculated as

$$\begin{aligned} & \sum_{i, \text{even}} \sum_{j, \text{even}} \sum_{k, \text{odd}} (\sin i \xi \cos i \xi') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta') \\ &= \sum_{i, \text{even}} (\sin i \xi \cos i \xi') \sum_{j, \text{even}} (\sin j \eta \sin j \eta') \sum_{k, \text{odd}} (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (21)$$

To calculate the summation in Eq. (19) (and to know the forms of all the elements of the Hamiltonian matrix), following four summations must be calculated as

$$\sum_{i, \text{odd}} \sin i \xi \cos i \xi' = \begin{cases} -2 \sin \xi \cos \xi' / (\cos 2\xi - \cos 2\xi'), & \text{if } (l \pm l') = \text{odd} \\ 0, & \text{if } (l \pm l') = \text{even} \end{cases} \quad (22)$$

$$\sum_{i, \text{even}} \sin i \xi \cos i \xi' = \begin{cases} -2 \sin \xi \cos \xi' / (\cos 2\xi - \cos 2\xi'), & \text{if } (l \pm l') = \text{odd} \\ 0, & \text{if } (l \pm l') = \text{even} \end{cases} \quad (23)$$

$$\sum_{i, \text{odd}} \sin i \xi \sin i \xi' = (\delta_{\xi, \xi'} + \delta_{\xi, \pi - \xi'}) \frac{N_A + 1}{4} \quad (24)$$

$$\sum_{i, \text{even}} \sin i \xi \sin i \xi' = (\delta_{\xi, \xi'} - \delta_{\xi, \pi - \xi'}) \frac{N_A + 1}{4} \quad (25)$$

With Eqs. (19) and (22)-(25), any elements of the Hamiltonian matrix can be calculated.

From Eqs. (22)-(25), the rules on mixing of cluster orbitals can be proved. In Eq. (14), for example, the summation can be separated as follows:

$$\begin{aligned} & \sum_{i,j,k} (\sin i \xi \cos i \xi') (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta') \\ &= \sum_{i, \text{even}} (\sin i \xi \cos i \xi') \sum_{j,k} (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta') \\ &+ \sum_{i, \text{odd}} (\sin i \xi \cos i \xi') \sum_{j,k} (\sin j \eta \sin j \eta') (\sin k \zeta \sin k \zeta'). \end{aligned} \quad (26)$$

From Eqs. (22) and (23), we can see that Eq. (26) is zero if $(l \pm l') = \text{even}$, i.e., the parities of l and l' of s -type cluster orbital and x -type one are same. So these two cluster orbitals can mix if their parities of l and l' are different from each other.

Concluding Remarks

As concluding remarks we like to discuss the merits and defects of our method. The major merit is that the limitation on the size of the cluster has been eliminated, for the method is analytic. If the cluster is infinite crystal, we can use the band theory of solid state physics. In this case, however, we cannot discuss surface phenomena, for the crystal has no surface. But cluster orbitals enable us to treat surface properties as well as bulk properties of solids. So, one can use this method, for instance, to study the adsorption phenomena on metal surfaces. However, our method has some

defects as: (1) the shape of cluster is limited, so the surface is also limited to (100) plane, and cluster must be of f.c.c. structure; (2) since only diagonal submatrices are diagonalized, i.e., since off-diagonal submatrices (interactions between cluster orbitals whose state indices differ from each other) are neglected, enough mixings are not included, esp. in case of p orbitals. The second defect arises from the fact that the state indices (l, m, n 's are not "good" quantum numbers.

The present work will be extended to two directions. One is to obtain, practically, several physical properties of metal clusters of varying sizes. As an example, our previous work⁹ on the hydrogen atoms in interstices of Pd, Ni, and Pt (all are of f.c.c. structure) clusters can be extended to large clusters. These results will be reported on forthcoming paper.¹⁰ The other is to modify our scheme to include more interactions and to obtain better solutions.

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Appendices

1. Finding the character of ψ_x^{lmn} under symmetry operation $\hat{C}_2(z)$

$$\begin{aligned} & \hat{C}_2(z) \psi_x^{lmn} \\ &= \hat{C}_2(z) N_0 \sum_{i,j,k} p_x(i, j, k) [\sin i \xi \sin j \eta \sin k \zeta] \\ &= N_0 \sum_{i,j,k} [\hat{C}_2(z) p_x(i, j, k)] [\sin i \xi \sin j \eta \sin k \zeta] \\ &= N_0 \sum_{i,j,k} [(-1) \cdot p_x(N_A + 1 - i, N_B + 1 - j, k)] [\sin i \xi \sin j \eta \sin k \zeta]. \end{aligned} \quad (A1)$$

If we replace $N_A + 1 - i$ and $N_B + 1 - j$ by i and j , respectively, the above equation can be written as

$$\begin{aligned} & \hat{C}_2(z) \psi_x^{lmn} \\ &= N_0 \sum_{i,j,k} [(-1) \cdot p_x(i, j, k)] [\sin(l\pi - i\xi) \sin(m\pi - j\eta) \sin k \zeta] \\ &= N_0 \sum_{i,j,k} [(-1) \cdot p_x(i, j, k)] [(-1)^{l+1} \cdot (-1)^{m+1} \sin i \xi \sin j \eta \sin k \zeta] \\ &= (-1) \cdot (-1)^{l+m} N_0 \sum_{i,j,k} [p_x(i, j, k)] [\sin i \xi \sin j \eta \sin k \zeta]. \end{aligned} \quad (A2)$$

$$\therefore \hat{C}_2(z) \psi_x^{lmn} = [(-1) \cdot (-1)^{l+m}] \psi_x^{lmn}. \quad (A3)$$

2. Deriving the terms representing interactions between the nearest neighbors

The number of the nearest neighbors of each atom corresponding to each of three planes — that is, xy -, yz - and xz -

planes — is four. We can decompose the terms representing the interactions between the nearest neighbors to three terms which results from three planes. We will consider only xy -plane. The formulae for other planes can be obtained similarly.

$$\begin{aligned} & (z^2/z^2) \Big|_{\substack{xy\text{-plane} \\ \text{the nearest neighbors}}} \\ &= E_{z^2, z^2(110)} N_0^2 \sum_{i,j,k} \sin i \xi \sin j \eta [\sin(i+1)\xi + \sin(i-1)\xi] \end{aligned}$$

$$\times [\sin(j+1)\eta + \sin(j-1)\eta] \sin k\xi \sin k\zeta \quad (\text{A4})$$

Additional terms arising from surface atoms, say $\sin(i-1)\xi$ in case of $i=1$, appear in Eq. (A4). However, $\sin(i-1)\xi=0$, so all of these terms are zero. Now, this equation can be simplified as

$$\begin{aligned} (z^2/z^2) \Big|_{\substack{\text{xy-plane} \\ \text{the nearest neighbors}}} \\ &= 4E_{z,z} \rho(110) N_0^2 \cos\xi \cos\eta \sum_{i,j,k} \sin^2 i\xi \sin^2 j\eta \sin^2 k\zeta \\ &= 4E_{z,z} \rho(110) \cos\xi \cos\eta. \end{aligned} \quad (\text{A5})$$

Similarly,

$$(z^2/z^2) \Big|_{\substack{\text{yz-plane} \\ \text{the nearest neighbors}}} = 4E_{z,z} \rho(011) \cos\eta \cos\xi, \quad (\text{A6})$$

and

$$(z^2/z^2) \Big|_{\substack{\text{xz-plane} \\ \text{the nearest neighbors}}} = 4E_{z,z} \rho(101) \cos\xi \cos\zeta. \quad (\text{A7})$$

$$\begin{aligned} \therefore (z^2/z^2) \Big|_{\substack{\text{the nearest neighbors}}} &= 4E_{z,z} \rho(110) \cos\xi \cos\eta \\ &+ 4E_{z,z} \rho(011) \cos\eta \cos\xi + 4E_{z,z} \rho(101) \cos\xi \cos\zeta. \end{aligned} \quad (\text{A8})$$

3. Derivation of terms representing interactions between the second nearest neighbors

The number of the second nearest neighbors of each atom corresponding to each of three axes – that is, x , y - and z -axes – is two. We can decompose the terms representing the interactions between the second nearest neighbors to three terms which result from three axes. We will consider only x -axis. The formulae for other can be obtained similarly.

$$\begin{aligned} (z^2/z^2) \Big|_{\substack{\text{x-axis} \\ \text{the second nearest neighbors}}} \\ &= E_{z,z} \rho(200) N_0^2 \left\{ \sum_{i,j,k} \sin^2 i\xi [\sin(i+2)\xi + \sin(i-2)\xi] \sin^2 j\eta \sin^2 k\zeta \right. \\ &\quad \left. - \sum_{\substack{j,k \\ j+k=\text{even}}} [\sin^2 \xi \sin(-\xi) + \sin(l\pi - \xi) \sin(l\pi + \xi)] \sin^2 j\eta \sin^2 k\zeta \right\} \end{aligned} \quad (\text{A9})$$

The form of Eq. (A9), dealing with interactions between the second nearest neighbors, is not so simple as Eq. (A4), dealing with interactions between the nearest neighbors. For surface atoms, the first part of Eq. (A9) contains additional terms which are not zero. Say, if $i=1$, $\sin(i-2)\xi = \sin(-\xi)$, and this is not zero. These terms originate from sites where no atom lies, say $(-2, 1, 1)$. So they must be excluded from the summation for the equality to hold. These excluded terms comprise the second part of the equation. This equation can be simplified as

$$\begin{aligned} (z^2/z^2) \Big|_{\substack{\text{x-axis} \\ \text{the second nearest neighbors}}} \\ &= E_{z,z} \rho(200) N_0^2 \left\{ 2 \cos 2\xi \sum_{i,j,k} \sin^2 i\xi \sin^2 j\eta \sin^2 k\zeta \right. \\ &\quad \left. + 2 \sin^2 \xi \sum_{\substack{j,k \\ j+k=\text{even}}} \sin^2 j\eta \sin^2 k\zeta \right\} \\ &= 2E_{z,z} \rho(200) \cos 2\xi + 4E_{z,z} \rho(200) \frac{\sin^2 \xi}{N_A + 1}. \end{aligned} \quad (\text{A10})$$

Similarly,

$$\begin{aligned} (z^2/z^2) \Big|_{\substack{\text{y-axis} \\ \text{the second nearest neighbors}}} \\ &= 2E_{z,z} \rho(020) \cos 2\eta + 4E_{z,z} \rho(020) \frac{\sin^2 \eta}{N_B + 1}, \end{aligned} \quad (\text{A11})$$

and

$$\begin{aligned} (z^2/z^2) \Big|_{\substack{\text{z-axis} \\ \text{the second nearest neighbors}}} \\ &= 2E_{z,z} \rho(002) \cos 2\zeta + 4E_{z,z} \rho(002) \frac{\sin^2 \zeta}{N_C + 1}. \end{aligned} \quad (\text{A12})$$

$$\begin{aligned} \therefore (z^2/z^2) \Big|_{\substack{\text{the second nearest neighbors}}} \\ &= 2E_{z,z} \rho(200) \cos 2\xi + 4E_{z,z} \rho(200) \frac{\sin^2 \xi}{N_A + 1} \\ &\quad + 2E_{z,z} \rho(020) \cos 2\eta + 4E_{z,z} \rho(020) \frac{\sin^2 \eta}{N_B + 1} \\ &\quad + 2E_{z,z} \rho(002) \cos 2\zeta + 4E_{z,z} \rho(002) \frac{\sin^2 \zeta}{N_C + 1}. \end{aligned} \quad (\text{A13})$$

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