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Symmetry-adapted cluster *f*-orbitals and a vector method for generally oriented *f*-orbital overlaps*

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The irreducible representations consisting of linear combinations of cluster atomic *f*-orbitals are obtained for $f\sigma$, $f\pi$, $f\delta$ and $f\phi$ orbitals in $M_3(D_{3h})$, $M_4(D_{4h})$, $M_4(T_d)$, $M_6(O_h)$ and $M_8(O_h)$ clusters. The charge overlap of any pair of two atoms in a cluster is decomposed in terms of a set of coefficients for the σ, π, δ, and ϕ overlaps, respectively. A vector method is devised for this decomposition which may be extended to any arbitrary orientation and to higher orbitals. The decomposition coefficients represent fundamental geometrical properties of the cluster and are applicable to clusters of arbitrary dimensions.

Key words: *f*-Orbitals — Metal clusters — Overlap integrals — LCAO-MO — Symmetry orbitals

1. Introduction

Metal clusters are coming into increasing interest to chemists. They are useful in understanding chemical bonding in metals, catalysis by metals and eventually the surface chemistry of metals. Many recent popular articles [1, 2] as well as scholarly books [3, 4] and reviews [5, 8] are available. It is therefore interesting to derive the molecular orbitals for these metal clusters in basic geometries. (Fig. 1). Such basic geometries are of course useful in crystal unit cells, such as face

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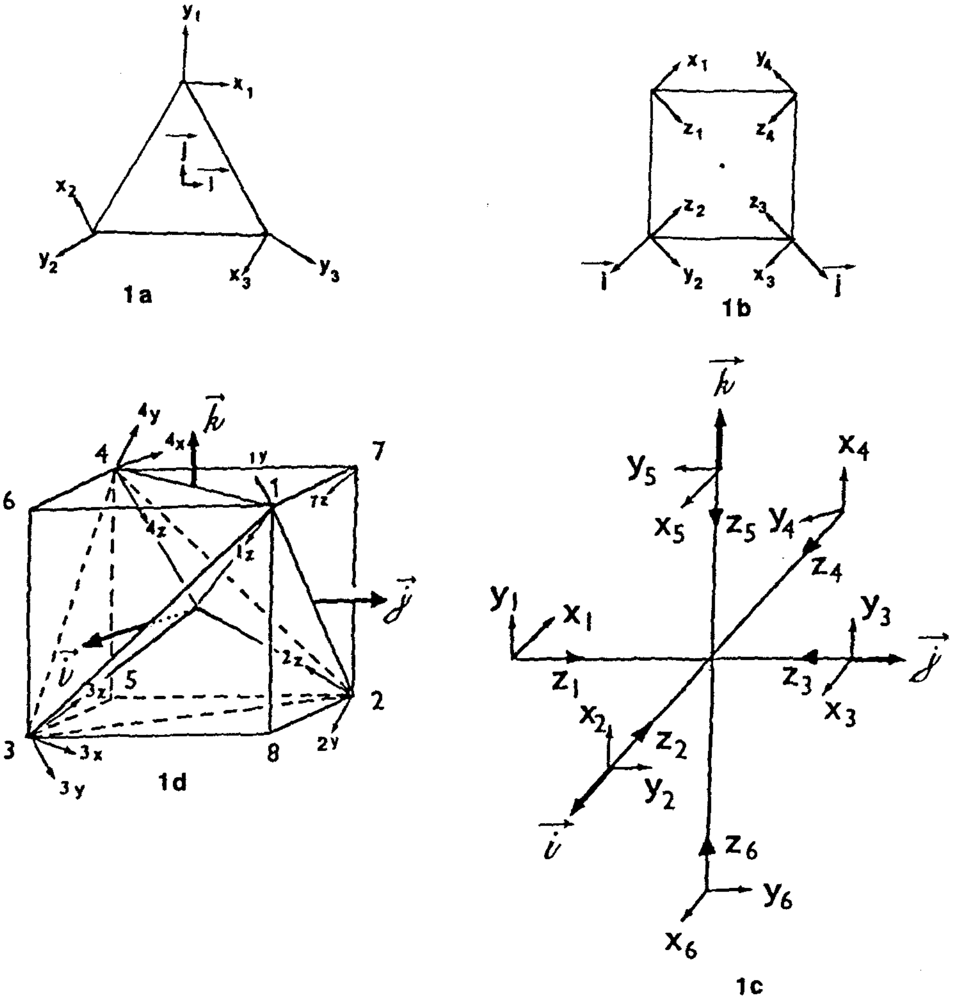

Fig. 1. Coordinate systems for clusters: $M_3(D_{3h})$ (1a); $M_4(D_{4h})$ (1b); $M_6(O_h)$ (1c) and $M_8(O_h)$ (1d). Specification of local coordinates in terms of the common unit vectors i, j, k at the origin are given in Table 1 and Refs. [9, 11, 12]

centered cube etc. In a recent work the writers [9] have derived the molecular orbitals consisting of up to *d*-atomic orbitals for $M_8(O_h)$, $M_4(T_d)$ and $M_6(O_h)$ clusters. We also considered the orientational problem for the overlap of up to *d*-orbitals. This work is to extend the derivation to *f*-atomic orbitals pertinent in heavy metals [10]. We shall derive here the symmetry adapted LCAO-MO for *f*-atomic orbitals of $M_3(D_{3h})$, $M_4(T_d)$, $M_4(D_{4h})$, $M_6(O_h)$ and $M_8(O_h)$ (Tables 2-7). We shall also elucidate the orientational problem of decomposing the general *f*-overlaps in terms of $f\sigma$, $f\pi$, $f\delta$ and $f\phi$ overlaps. While some overlap integrals may be computed in *ab initio* machine calculations, explicit overlaps are needed for understanding bonding and symmetry of electronic distributions.

Table 1. Local coordinate systems[a,b] and atomic labels for the $M_3(D_{3h})$ and $M_4(D_{4h})$ clusters

$M_3(D_{3h})$	$M_4(D_{4h})$
$x_1 = (\ 1 \quad 0 \quad 0)$	$x_1 = (-1 \quad 0 \quad 0)$
$y_1 = (\ 0 \quad 1 \quad 0)$	$y_1 = (\ 0 \quad 0 \quad 1)$
$z_1 = (\ 0 \quad 0 \quad 1)$	$z_1 = (\ 0 \quad 1 \quad 0)$
$x_2 = (-\frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad 0)$	$x_2 = (\ 0 \quad 0 \quad 1)$
$y_2 = (-\frac{\sqrt{3}}{2} \quad -\frac{1}{2} \quad 0)$	$y_2 = (\ 0 \quad 1 \quad 0)$
$z_2 = (\ 0 \quad 0 \quad 1)$	$z_2 = (-1 \quad 0 \quad 0)$
$x_3 = (-\frac{1}{2} \quad -\frac{\sqrt{3}}{2} \quad 0)$	$x_3 = (1 \quad 0 \quad 0)$
$y_3 = (\ \frac{\sqrt{3}}{2} \quad -\frac{1}{2} \quad 0)$	$y_3 = (0 \quad 0 \quad 1)$
$z_3 = (\ 0 \quad 0 \quad 1)$	$z_3 = (0 \quad -1 \quad 0)$
	$x_4 = (0 \quad 0 \quad 1)$
	$y_4 = (0 \quad -1 \quad 0)$
	$z_4 = (1 \quad 0 \quad 0)$

[a] In terms of projection on the local parallels to the common coordinate $(\vec{i}, \vec{j}, \vec{k})$

[b] See Figs. 1a and 1b. Coordinates for $M_6(O_h)$ are the same as those given by Purcell and Kotz (Ref. [12]). Coordinates for $M_4(T_d)$, $M_8(O_h)$ are the same as those of Watanabe (Ref. [11]). See also an earlier work of the authors (Ref. [9])

Table 2. Summary of irreducible representations of *f*-orbitals[a] in various clusters

	$M_3(D_{3h})$	$M_4(D_{4h})$	$M_4(T_d)$	$M_6(O_h)$	$M_8(O_h)$
$f\sigma(d_z^2, P_z, s)$	$a_2''; e''$	$a_{1g}; b_{1g};$ e_u	$a_1; t_2$	$a_{1g}; e_g;$ t_{1u}	$a_{1g}; a_{2u};$ $t_{1u}; t_{2g}$
$f\pi_x$ (d_{xz}, P_x)	$a_2'; e'$	$a_{2g}; b_{2g};$ $a_{2u}; b_{2u};$ $e_g; e_u$	$e; t_1;$ t_2	$t_{1g}; t_{2g};$ $t_{1u}; t_{2u}$	$e_g; e_u;$ $t_{1g}; t_{1u};$ $t_{2g}; t_{2u}$
$f\pi_y$ (d_{yz}, P_y)	$a_1'; e'$				
$f\delta_{xy}$ (d_{xy})	$a_1''; e''$	$a_{1g}; b_{1g};$ $a_{1u}; b_{1u};$	$e_1; t_1$ t_2	$a_{2g}; a_{2u};$ $e_g; e_u;$ $t_{2g}; t_{2u}$	$e_g; e_u;$ $t_{1g}; t_{1u};$ $t_{2g}; t_{2u}$
$f\delta_{x^2-y^2}$ $(d_{x^2-y^2})$	$a_2''; e''$	$e_g; e_u$			
$f\phi_x$	$a_2'; e'$	$a_{2g}; b_{2g};$	$a_1; a_2;$	$t_{1g}; t_{1u};$	$a_{1g}; a_{1u};$ $a_{2g}; a_{2u};$
$f\phi_y$	$a_1'; e'$	$a_{2u}; b_{2u};$ $e_g; e_u$	$t_1; t_2$	$t_{2g}; t_{2u}$	$t_{1g}; t_{1u};$ $t_{2g}; t_{2u}$

[a] *d*, *p*, and *s* orbitals that transform similarly are also shown (in parenthesis). $f\delta$, $f\pi$ and $f\sigma$ LCAO-MO may also be obtained from correlation to *d*, *p*, *s* orbitals. The latter serve as a double check. $f\phi$ may have very different transformations from those of P_x and P_y

Table 3. Symmetry adapted f-orbitals in a $M_3(D_{3h})$ cluster[a]

Λ	LCAO	D_{3h} symmetry	Normalization constant, $N=$	"Energy" E^b $\times N^{-2}$
σ	$f\sigma_1+f\sigma_2+f\sigma_3$	a_2''	$(3+6S_{\sigma\sigma}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\sigma\sigma}^{1,2})$
	$f\sigma_3-f\sigma_2$	e_{xz}''		
	$2f\sigma_1-f\sigma_2-f\sigma_3$	e_{yz}''	$(2-2S_{\sigma\sigma}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\sigma\sigma}^{1,2})$
π_x	$f\eta_1+f\eta_2+f\eta_3$	a_2'	$(3+6S_{\eta\eta}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\eta\eta}^{1,2})$
	$2f\eta_1-f\eta_2-f\eta_3$	e_x'		
	$f\eta_2-f\eta_3$	e_y'	$(2-2S_{\eta\eta}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\eta\eta}^{1,2})$
π_y	$f\xi_1+f\xi_2+f\xi_3$	a_1'	$(3+6S_{\xi\xi}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\xi\xi}^{1,2})$
	$f\xi_3-f\xi_2$	e_x'		
	$2f\xi_1-f\xi_2-f\xi_3$	e_y'	$(2-2S_{\xi\xi}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\xi\xi}^{1,2})$
δ_{xy}	$f\zeta_1+f\zeta_2+f\zeta_3$	a_1''	$(3+6S_{\zeta\zeta}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\zeta\zeta}^{1,2})$
	$2f\zeta_1-f\zeta_2-f\zeta_3$	e_{xz}''		
	$f\zeta_2-f\zeta_3$	e_{yz}''	$(2-2S_{\zeta\zeta}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\zeta\zeta}^{1,2})$
$\delta_{x^2-y^2}$	$f\varepsilon_1+f\varepsilon_2+f\varepsilon_3$	a_2''	$(3+6S_{\varepsilon\varepsilon}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\varepsilon\varepsilon}^{1,2})$
	$f\varepsilon_3-f\varepsilon_2$	e_{xz}''		
	$2f\varepsilon_1-f\varepsilon_2-f\varepsilon_3$	e_{yz}''	$(2-2S_{\varepsilon\varepsilon}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\varepsilon\varepsilon}^{1,2})$
ϕ_x	$f\phi_{x1}+f\phi_{x2}+f\phi_{x3}$	a_2'	$(3+6S_{\phi x\phi x}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\phi x\phi x}^{1,2})$
	$2f\phi_{x1}-f\phi_{x2}-f\phi_{x3}$	e_x'		
	$f\phi_{x2}-f\phi_{x3}$	e_y'	$(2-2S_{\phi x\phi x}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\phi x\phi x}^{1,2})$
ϕ_y	$f\phi_{y1}+f\phi_{y2}+f\phi_{y3}$	a_1'	$(3+6S_{\phi y\phi y}^{1,2})^{-1/2}$	$(3\alpha+6\beta_{\phi y\phi y}^{1,2})$
	$f\phi_{y3}-f\phi_{y2}$	e_x'		
	$2f\phi_{y1}-f\phi_{y2}-f\phi_{y3}$	e_y'	$(2-2S_{\phi y\phi y}^{1,2})^{-1/2}$	$(2\alpha-2\beta_{\phi y\phi y}^{1,2})$

[a] See Eq. (1) for the definition of f-orbitals and Fig. 1a for the local coordinates. Table 8 for the decomposition of the overlap integrals. If β is taken to be proportional to overlap, its decomposition is the same as for overlap integrals

[b] The energy expression is strictly valid only if the symmetry is unique and no mixing is involved (e.g. mixing of $\sigma(a_2'')$ and $\delta_{x^2-y^2}(a_2'')$). α is the atomic coulomb integral which may be approximated by the valence orbital ionization energy. β is the resonance integral

Table 4. Symmetry adapted f-orbitals in a $M_4(D_{4h})$ cluster[a]

Λ	LCAO	D_{4h} symmetry	Normalization constant $N=$	"Energy" E $\times N^{-2}$
σ	$f\sigma_1+f\sigma_2+f\sigma_3+f\sigma_4$	A_{1g}	$(4+8S_{\sigma\sigma}^{1,2}+4S_{\sigma\sigma}^{1,3})^{-1/2}$	Express constant
	$f\sigma_1-f\sigma_2+f\sigma_3-f\sigma_4$	B_{1g}	$(4-8S_{\sigma\sigma}^{1,2}+4S_{\sigma\sigma}^{1,3})^{-1/2}$	term in α. Replace S
	$f\sigma_2-f\sigma_4; f\sigma_3-f\sigma_1$	E_u	$(2-2S_{\sigma\sigma}^{1,3})^{-1/2}$	with β and square
$\pi_x=\eta$	$f\eta_1+f\xi_2+f\eta_3+f\xi_4$	B_{2g}	$(4+8S_{\eta\xi}^{1,2}+4S_{\eta\eta}^{1,3})^{-1/2}$	Express constant
$\pi_y=\xi$	$f\eta_1-f\xi_2+f\eta_3-f\xi_4$	A_{2g}	$(4-8S_{\eta\xi}^{1,2}+4S_{\eta\eta}^{1,3})^{-1/2}$	term in α. Replace S
	$f\xi_1+f\eta_2+f\xi_3+f\eta_4$	A_{2u}	$(4+8S_{\xi\eta}^{1,2}+4S_{\xi\xi}^{1,3})^{-1/2}$	with β and square
	$f\xi_1-f\eta_2+f\xi_3-f\eta_4$	B_{2u}	$(4-8s_{\xi\eta}^{1,2}+4s_{\xi\xi}^{1,2})^{-1/2}$	
	$f\eta_2-f\eta_4$: $f\xi_3-f\eta_1$	E_g	$(2-2S_{\eta\eta}^{2,4})^{-1/2}$	
	$f\eta_3-f\eta_1$: $f\xi_2-f\xi_4$	E_u	$(2-2S_{\eta\eta}^{1,3})^{-1/2}$	

Table 4 (continued)

Λ	LCAO	D_{4h} symmetry	Normalization constant $N =$	"Energy" E $\times N^{-2}$
$\delta_{xy} = \zeta$	$f\varepsilon_1 + f\varepsilon_2 + f\varepsilon_3 + f\varepsilon_4$	B_{1g}	$(4+8S^{1,2}_{\varepsilon\varepsilon}+4S^{1,3}_{\varepsilon\varepsilon})^{-1/2}$	Express constant term in α. Replace S with β and square
$\delta_{x^2-y^2} = \varepsilon$	$f\zeta_1 + f\zeta_2 + f\zeta_3 + f\zeta_4$	B_{1u}	$(4+8S^{1,2}_{\zeta\zeta}+4S^{1,3}_{\zeta\zeta})^{-1/2}$	
	$f\varepsilon_1 - f\varepsilon_2 + f\varepsilon_3 - f\varepsilon_4$	A_{1g}	$(4-8S^{1,2}_{\varepsilon\varepsilon}+4S^{1,3}_{\varepsilon\varepsilon})^{-1/2}$	
	$f\zeta_1 - f\zeta_2 + f\zeta_3 - f\zeta_4$	A_{1u}	$(4-8S^{1,2}_{\zeta\zeta}+4S^{1,3}_{\zeta\zeta})^{-1/2}$	
	$f\zeta_3 - f\zeta_1; f\zeta_2 - f\zeta_4$	E_g	$(2-2S^{1,3}_{\zeta\zeta})^{-1/2}$	
	$f\varepsilon_4 - f\varepsilon_2; f\varepsilon_3 - f\varepsilon_1$	E_u	$(2-2S^{1,3}_{\varepsilon\varepsilon})^{-1/2}$	
ϕ_x	$f\phi_{x1} + f\phi_{y2} + f\phi_{x3} + f\phi_{y4}$	A_{2g}	$(4+8S^{1,2}_{x,y}+4S^{1,3}_{xx})^{-1/2}$	Express constant term in α. Replace S with β and square
ϕ_y	$f\phi_{y1} - f\phi_{x2} + f\phi_{y3} - f\phi_{x4}$	A_{2u}	$(4-8S^{1,2}_{yx}+4S^{1,3}_{yy})^{-1/2}$	
	$f\phi_{x1} - f\phi_{y2} + f\phi_{x3} - f\phi_{y4}$	B_{2g}	$(4-8S^{1,2}_{x,y}+4S^{1,3}_{xx})^{-1/2}$	
	$f\phi_{y1} + f\phi_{x2} + f\phi_{y3} + f\phi_{x4}$	B_{2u}	$(4+8S^{1,2}_{y,x}+4S^{1,3}_{yy})^{-1/2}$	
	$f\phi_{x2} - f\phi_{x4}; f\phi_{y3} - f\phi_{y1}$	E_g	$(2-S^{1,3}_{y,y})^{-1/2}$	
	$f\phi_{x1} - f\phi_{x3}; f\phi_{y4} - f\phi_{y2}$	E_u	$(2-S^{1,3}_{x,x})^{-1/2}$	

[a] See Eq. (1) for the definition of *f*-orbitals and Fig. 1b for the local coordinates. See Table 9 for the decomposition of the overlap integrals (and the assumed similar decomposition of the resonance integrals β). α is the coulomb integral, see Table 3

Table 5. Symmetry adapted *f*-orbitals in a $M_4(T_d)$ cluster[a]

Λ	LCAO	T_d	Normalization constant
σ	Same combination[b] as for d_z^2, P_z or S	a_1	$(4+12S^{1,2}_{\sigma\sigma})^{-1/2}$
		t_2	$(4-4S^{1,2}_{\sigma\sigma})^{-1/2}$
π_x	Same combination as for $(d_{xz}d_{yz}), (P_x, P_y)$	e	$(4+8S^{1,2}_{\xi\xi}+4S^{1,4}_{\xi\xi})^{-1/2}$
π_y		t_1	$(4-8S^{1,2}_{\eta\eta}+4S^{1,4}_{\eta\eta})^{-1/2}$
		t_2	$(4-8S^{1,2}_{\xi\xi}+4S^{1,4}_{\xi\xi})^{-1/2}$
δ_{xy}	Same combination as for $d\delta_{xy}, d\delta_{x^2-y^2}$	e	$(4+8S^{1,2}_{\varepsilon\varepsilon}+4S^{1,4}_{\varepsilon\varepsilon})^{-1/2}$
$\delta_{x^2-y^2}$		t_1	$(4-8S^{1,2}_{\zeta\zeta}+4S^{1,4}_{\zeta\zeta})^{-1/2}$
		t_2	$(4-8S^{1,2}_{\varepsilon\varepsilon}+4S^{1,4}_{\varepsilon\varepsilon})^{-1/2}$
ϕ_x	$f\phi_{x1} + f\phi_{x2} + f\phi_{x3} + f\phi_{x4}$	A_2	$(4+12S^{1,2}_{\phi x\phi x})^{-1/2}$
	$f\phi_{x1} - f\phi_{x2} + f\phi_{x3} - f\phi_{x4}$	T_{1x}	$(4-4S^{1,2}_{\phi x\phi x})^{-1/2}$
	$f\phi_{x1} + f\phi_{x2} - f\phi_{x3} - f\phi_{x4}$	T_{1y}	
	$f\phi_{x1} - f\phi_{x2} - f\phi_{x3} + f\phi_{x4}$	T_{1z}	
ϕ_y	$f\phi_{y1} + f\phi_{y2} + f\phi_{y3} + f\phi_{y4}$	A_1	$(4+12S^{1,2}_{\phi y\phi y})^{-1/2}$
	$f\phi_{y1} - f\phi_{y2} + f\phi_{y3} - f\phi_{y4}$	$T_{2\xi}$	$(4-4S^{1,2}_{\phi y\phi y})^{-1/2}$
	$f\phi_{y1} + f\phi_{y2} - f\phi_{y3} - f\phi_{y4}$	$T_{2\eta}$	
	$f\phi_{y1} - f\phi_{y2} - f\phi_{y3} + f\phi_{y4}$	$T_{2\zeta}$	

[a] See Eq. (1) for the definition of *f*-orbitals and Fig. 1d for the local coordinates

[b] The linear combiatnions for *p*-orbitals have been given by Watanabe (Ref. [11]), those for *d*-orbitals have been given by Chiu and Wang (Ref. [9])

Table 6. Symmetry adapted *f*-orbitals in a $M_6(O_h)$ cluster[a]

Λ	LCAO	O_h	Normalization constant
σ	Same combination[b] as for d_{z^2},	a_{1g}	$(6+6S^{1,3}_{\sigma\sigma}+24S^{1,5}_{\sigma\sigma})^{-1/2}$
	P_z or S	e_g	$(4+S^{1,3}_{\sigma\sigma}-8S^{1,5}_{\sigma\sigma})^{-1/2}$
		t_{1u}	$(2-S^{1,3}_{\sigma\sigma})^{-1/2}$
π_x	Same combination as for	t_{1g}	$(4-4S^{1,3}_{\xi\xi}-8S^{1,5}_{\xi\xi})^{-1/2}$
π_y	$(d_{xz}, d_{yz}), (P_x, P_y)$	t_{2g}	$(4-4S^{1,3}_{\xi\xi}+8S^{1,5}_{\xi\xi})^{-1/2}$
		t_{1u}	$(4-4S^{1,3}_{\eta\eta}-8S^{1,5}_{\eta\eta})^{-1/2}$
		t_{2u}	$(4-4S^{1,3}_{\eta\eta}+8S^{1,5}_{\eta\eta})^{-1/2}$
δ_{xy}	Same combination as for	a_{2g}	$(6-24S^{1,5}_{\varepsilon\varepsilon}+6S^{1,3}_{\varepsilon\varepsilon})^{-1/2}$
$\delta_{x^2-y^2}$	$(d\delta_{xy}, d\delta_{x^2-y^2})$	a_{2u}	$(6-24S^{1,5}_{\zeta\zeta}+6S^{1,3}_{\zeta\zeta})^{-1/2}$
		e_g	$(4-8S^{1,2}_{\varepsilon\varepsilon}+4S^{1,3}_{\varepsilon\varepsilon})^{-1/2}$
		e_u	$(4-8S^{1,2}_{\zeta\zeta}+4S^{1,3}_{\zeta\zeta})^{-1/2}$
		t_{2g}	$(2-S^{5,6}_{\zeta\zeta})^{-1/2}$
		t_{2u}	$(2-S^{5,6}_{\varepsilon\varepsilon})^{-1/2}$
ϕ_x	$\phi_{x1}-\phi_{x3}-\phi_{x5}-\phi_{x6}$	t_{1ux}	$(4-8S^{1,5}_{\phi x\phi x}+4S^{5,6}_{\phi x\phi x})^{-1/2}$
ϕ_y	$\phi_{y2}-\phi_{y4}-\phi_{y5}+\phi_{y6}$	t_{1uy}	
	$\phi_{y1}+\phi_{y3}-\phi_{x2}-\phi_{x4}$	t_{1uz}	
	$\phi_{y1}-\phi_{y3}-\phi_{y5}-\phi_{y6}$	t_{1gx}	$(4-8S^{1,5}_{\phi y\phi y}+4S^{5,6}_{\phi y\phi y})^{-1/2}$
	$\phi_{x2}-\phi_{x4}-\phi_{x5}+\phi_{x6}$	t_{1gy}	
	$\phi_{x1}+\phi_{x3}+\phi_{y2}+\phi_{y4}$	t_{1gz}	
	$\phi_{y1}-\phi_{y3}+\phi_{y5}+\phi_{y6}$	$t_{2g\xi}$	$(4+8S^{1,5}_{\phi y\phi y}+4S^{5,6}_{\phi y\phi y})^{-1/2}$
	$\phi_{x2}-\phi_{x4}+\phi_{x5}-\phi_{x6}$	$t_{2g\eta}$	
	$\phi_{x1}+\phi_{x3}-\phi_{y2}-\phi_{y4}$	$t_{2g\zeta}$	
	$\phi_{x1}-\phi_{x3}+\phi_{x5}+\phi_{x6}$	$t_{2u\xi}$	$(4+8S^{1,5}_{\phi x\phi x}+4S^{5,6}_{\phi x\phi x})^{-1/2}$
	$\phi_{y2}-\phi_{y4}+\phi_{y5}-\phi_{y6}$	$t_{2u\eta}$	
	$\phi_{y1}+\phi_{y3}+\phi_{x2}+\phi_{x4}$	$t_{2u\zeta}$	

[a] See Eq. (1) for the definition of *f*-orbitals and Fig. 1c for the local coordinates
[b] The linear combinations of *p*-orbitals have been given by Watanabe (Ref. [11]). Those for *d*-orbitals have been given by Chiu and Wang (Ref. [9])

Table 7. Symmetry adapted *f*-orbitals in a $M_8(O_h)$ cluster[a,b]

Λ	LCAO	O_h	Normalization constant N^2
ϕ_x	$f\phi_{x1}+f\phi_{x2}+f\phi_{x3}+f\phi_{x4}-f\phi_{x5}-f\phi_{x6}-f\phi_{x7}-f\phi_{x8}$	A_{2g}	$8+24S^{1,2}_{xx}-16S^{1,6}_{xx}-8S^{1,5}_{xx}$
	$f\phi_{x1}+f\phi_{x2}+f\phi_{x3}+f\phi_{x4}+f\phi_{x5}+f\phi_{x6}+f\phi_{x7}+f\phi_{x8}$	A_{1u}	$8+24S^{1,2}_{xx}+16S^{1,6}_{xx}+8S^{1,5}_{xx}$
	$f\phi_{x1}-f\phi_{x2}+f\phi_{x3}-f\phi_{x4}-f\phi_{x5}+f\phi_{x6}-f\phi_{x7}+f\phi_{x8}$	T_{1gx}	$8-8S^{1,2}_{xx}+8S^{1,6}_{xx}-8S^{1,5}_{xx}$
	$f\phi_{x1}+f\phi_{x2}-f\phi_{x3}-f\phi_{x4}-f\phi_{x5}-f\phi_{x6}+f\phi_{x7}+f\phi_{x8}$	T_{1gy}	
	$f\phi_{x1}-f\phi_{x2}-f\phi_{x3}+f\phi_{x4}-f\phi_{x5}+f\phi_{x6}+f\phi_{x7}-f\phi_{x8}$	T_{1gz}	
	$f\phi_{x1}-f\phi_{x2}+f\phi_{x3}-f\phi_{x4}+f\phi_{x5}-f\phi_{x6}+f\phi_{x7}-f\phi_{x8}$	$T_{2u\xi}$	$8-8S^{1,2}_{xx}-8S^{1,6}_{xx}+8S^{1,5}_{xx}$
	$f\phi_{x1}+f\phi_{x2}-f\phi_{x3}-f\phi_{x4}+f\phi_{x5}+f\phi_{x6}-f\phi_{x7}-f\phi_{x8}$	$T_{2u\eta}$	
	$f\phi_{x1}-f\phi_{x2}-f\phi_{x3}+f\phi_{x4}+f\phi_{x5}-f\phi_{x6}-f\phi_{x7}+f\phi_{x8}$	$T_{2u\zeta}$	

Table 7 (continued)

Λ	LCAO	O_h	Normalization constant N^2
ϕy	$f\phi_{y1}+f\phi_{y2}+f\phi_{y3}+f\phi_{y4}+f\phi_{y6}+f\phi_{y7}+f\phi_{y8}$	A_{1g}	$8+24S_{yy}^{1,2}+16S_{yy}^{1,6}+8S_{yy}^{1,5}$
	$f\phi_{y1}+f\phi_{y2}+f\phi_{y3}+f\phi_{y4}-f\phi_{y5}-f\phi_{y6}-f\phi_{y7}-f\phi_{y8}$	A_{2u}	$8+24S_{yy}^{1,2}-16S_{yy}^{1,6}-8S_{yy}^{1,5}$
	$f\phi_{y1}-f\phi_{y2}+f\phi_{y3}-f\phi_{y4}+f\phi_{y5}-f\phi_{y6}+f\phi_{y7}-f\phi_{y8}$	$T_{2g\xi}$	$8-8S_{yy}^{1,2}-8S_{yy}^{1,6}+8S_{yy}^{1,5}$
	$f\phi_{y1}+f\phi_{y2}-f\phi_{y3}-f\phi_{y4}+f\phi_{y5}+f\phi_{y6}-f\phi_{y7}-f\phi_{y8}$	$T_{2g\eta}$	
	$f\phi_{y1}-f\phi_{y2}-f\phi_{y3}+f\phi_{y4}+f\phi_{y5}-f\phi_{y6}-f\phi_{y7}+f\phi_{y8}$	$T_{2g\zeta}$	
	$f\phi_{y1}-f\phi_{y2}+f\phi_{y3}-f\phi_{y4}-f\phi_{y5}+f\phi_{y6}-f\phi_{y7}+f\phi_{y8}$	T_{1ux}	$8-8S_{yy}^{1,2}+8S_{yy}^{1,6}-8S_{yy}^{1,5}$
	$f\phi_{y1}+f\phi_{y2}-f\phi_{y3}-f\phi_{y4}-f\phi_{y5}-f\phi_{y6}+f\phi_{y7}+f\phi_{y8}$	T_{1uy}	
	$f\phi_{y1}-f\phi_{y2}-f\phi_{y3}+f\phi_{y4}-f\phi_{y5}+f\phi_{y6}+f\phi_{y7}-f\phi_{y8}$	T_{1uz}	

[a] See Eq. (1) for the definition of *f*-orbitals and Fig. 1d for the local coordinates

[b] $f\sigma$, $f\pi$ and $f\delta$ have the same combinations as $d\sigma$, $d\pi$ and $d\delta$ given by Chiu and Wang (Ref. [9])

Such symmetry adapted orbitals and overlaps are available thus far mostly in *p* or *d* orbitals [11-20] or in two-center situations.

The importance of *f* orbitals have been discussed recently for example by Jørgensen [19]. But, the computation [21, 22] of *f*-overlaps and the related tabulation [23], mostly apply only to the diatomic situation with parallel sets of local coordinates at two centers.

In a general cluster of atoms it is impractical to choose parallel local coordinates for *all* of the atoms because this will complicate the transformation of these under symmetry operations. The orientational problem is especially difficult for *f* orbitals which require rotational transformation matrices [24, 25] of the third rank [26]. When combination of atoms (e.g. in the M_6 cluster there are $6\times5/2=15$ pairs) and combination of orbitals (e.g. $7\times7=49$ for each pair of atoms with each atom having seven *f* orbitals) are large ($15\times49=735$), the choice of such large sets of Euler angles [14, 24, 25] is not only mind-boggling but also susceptible to error. Therefore we like to devise a method to solve this orientation problem—a vector method that can be adapted to the computer for efficiency and accuracy. Furthermore the principle of this method can be extended to $g(l=4)$, $h(l=5)$ waves etc. and can be extended to any arbitrary geometrical arrangement of atoms. The LCAO-MO's are also useful in correlation to united-atom or Rydberg orbitals of the clusters.

2. The vector method for *f*-orbital projection and overlaps

For the transformation in point groups and for orientational projections we omit the common radial part of the *f*-orbital. We consider only the real angular parts which are proportional to the linear combination of spherical harmonics of the third rank as follows:

$$\begin{aligned}
f\sigma &= \frac{\sqrt{7}}{2}\, z(5z^2-3r^2) = \frac{\sqrt{7}}{2}\, z(2z^3-3zx^2-3zy^2) \cong \sqrt{4\pi}\, Y_3^0, \\
f\pi_x &= \sqrt{\frac{21}{8}}\, x(5z^2-r^2) = \sqrt{\frac{21}{8}}\, x(4z^2-x^2-y^2) \equiv f\eta \cong -\sqrt{2\pi}(Y_3^1 - Y_3^{-1}), \\
f\pi_y &= \sqrt{\frac{21}{8}}\, y(5z^2-r^2) = \sqrt{\frac{21}{8}}\, y(4z^2-x^2-y^2) \equiv f\xi \cong \mathrm{i}\sqrt{2\pi}(Y_3^1 + Y_3^{-1}), \\
f\delta_{xy} &= \sqrt{\frac{105}{4}}\, 2xyz \equiv f\zeta \cong -\mathrm{i}\sqrt{2\pi}(Y_3^2 - Y_3^{-2}), \qquad (1) \\
f\delta_{x^2-y^2} &= \sqrt{\frac{105}{4}}\, z(x^2-y^2) \equiv f\varepsilon \cong \sqrt{2\pi}(Y_3^2 + Y_3^{-2}), \\
f\phi_x &= \sqrt{\frac{35}{8}}\, x(x^2-3y^2) \cong -\sqrt{2\pi}(Y_3^3 - Y_3^{-3}), \\
f\phi_y &= \sqrt{\frac{35}{8}}\, y(3x^2-y^2) \cong \mathrm{i}\sqrt{2\pi}(Y_3^3 + Y_3^{-3}).
\end{aligned}$$

These are the f-orbitals in terms of the local coordinates. We choose the center of the cluster as the origin for a cluster-common coordinate system with unit vectors $\vec{i} = (1, 0, 0)$, $\vec{j} = (0, 1, 0)$ and $\vec{k} = (0, 0, 1)$. The local coordinate axes of a given atom may be defined in terms of the local parallels to these unit vectors. For $M_3(D_{3h})$ and $M_4(D_{4h})$ cluster, the orientations of atomic local axes are given in Table 1. They correspond to the designation in Fig. 1. The local axes for $M_4(Td)$, $M_8(O_h)$ are the same as in an earlier paper [9] and in Watanabe [11], the latter gave cluster orbitals up to p-orbitals. The local axes for $M_6(O_h)$ are the same as in Purcell and Kotz [12] who gave some of the cluster d-orbitals which we have refined [9]. Thus each local coordinate x, y, or z is a three-component vector quantity or a row (or column) vector. For a pair of atoms whose overlap is considered, we define a pair-common interatomic vector coordinate system $\vec{R}_1$, $\vec{R}_2$ and $\vec{R}_3$, where $\vec{R}_3$ is the $p\sigma_z$ overlap direction and $\vec{R}_1$, $\vec{R}_2$ are the $p\pi_x$ and $p\pi_y$ directions respectively. The $\vec{R}$'s are in a right-handed arrangement. In terms of the cluster-common coordinates $\vec{i}$, $\vec{j}$ and $\vec{k}$, each $\vec{R}_1$ or $\vec{R}_2$ or $\vec{R}_3$ is again a three-component vector quantity.

The local atomic coordinates of atom A, X_A, Y_A, Z_A are decomposed in terms of the pair-common coordinates as follows:

$$\vec{A}_1 = X_A = P_{11}\vec{R}_1 + P_{12}\vec{R}_2 + P_{13}\vec{R}_3 \qquad (2a)$$

$$\vec{A}_2 = Y_A = P_{21}\vec{R}_1 + P_{22}\vec{R}_2 + P_{23}\vec{R}_3 \qquad (2b)$$

$$\vec{A}_3 = Z_A = P_{31}\vec{R}_1 + P_{32}\vec{R}_2 + P_{33}\vec{R}_3 \qquad (2c)$$

The set of three coefficients in (2a) (or 2b or 2c) may be solved from three simultaneous equations arising from the three vector components.

To find the σ, π, δ or ϕ overlap we need to decompose the f orbital in terms of the above components in the pair-common interatomic coordinate system, viz for an arbitrary f orbital on atom A,

$$\begin{aligned} f_{\mathrm{A}} = \sum_{\nu} C_\nu r^3 Y_3^\nu(\theta_{\mathrm{A}}\Phi_{\mathrm{A}}) &= \mathrm{A}_S \frac{\sqrt{7}}{2}(2R_3^3 - 3R_3R_2^2 - 3R_3R_1^2) \\ &+ \mathrm{A}P_x\sqrt{\frac{21}{8}}R_1(4R_3^2 - R_1^2 - R_2^2) + \mathrm{A}P_y\sqrt{\frac{21}{8}}R_2(4R_3^2 - R_1^2 - R_2^2) \\ &+ \mathrm{A}D_{xx}\sqrt{\frac{105}{4}}R_3(R_1^2 - R_2^2) + \mathrm{A}D_{xy}\sqrt{\frac{105}{4}}2R_1R_2R_3 \\ &+ \mathrm{A}F_x\sqrt{\frac{35}{8}}(R_1^2 - 3R_2^2)R_1 + \mathrm{A}F_y\sqrt{\frac{35}{8}}(3R_1^2 - R_2^2)R_2 \\ = \sum_{\nu} C_\nu r^3 \sum_{\mu} D^3_{\mu\nu}(\alpha\beta\gamma) Y_3^\mu(\Theta\Phi), & \end{aligned} \tag{3}$$

where A_S, $\mathrm{A}P_x$, $\mathrm{A}P_y$, $\mathrm{A}D_{xx}$, $\mathrm{A}D_{xy}$, $\mathrm{A}F_x$ and $\mathrm{A}F_y$ stand for coefficients for σ, π_x, π_y, $\delta_{x^2-y^2}$, δ_{xy}, ϕ_x and ϕ_y projections. These coefficients are related to the rotation matrices (Eq. (9) below). C_ν is the coefficient for the linear combination of complex f-orbitals to get real orbitals. The Euler angles α, β, γ are for rotational transformation from the interatomic coordinates to the local coordinates. $D^3_{\mu\nu}$ is

Table 8. Atomic *f*-overlap between $M_3(D_{3h})$ cluster orbitals[a]

$S^{i,j}_{k1}$	F_{SG}	F_{PI}	F_{DL}	F_F	Equivalent to $S_{1,k}$	Equivalent to $S_{k,1}$
$S^{1,2}_{\sigma\sigma}$	0.0000	0.3750	0.0000	0.6250		(1, 3) (2, 3)
$S^{1,2}_{\eta\eta}$	−0.0937	−0.0469	−0.1562	−0.7030		(1, 3) (2, 3)
$S^{1,2}_{\xi\xi}$	0.2812	0.0156	0.4687	0.2343		(1, 3) (2, 3)
$S^{1,2}_{\zeta\zeta}$	0.0000	−0.4687	−0.2499	−0.2812		(1, 3) (2, 3)
$S^{1,2}_{\varepsilon\varepsilon}$	0.0000	0.1562	0.7499	0.0937		(1, 3) (2, 3)
$S^{1,2}_{\sigma\zeta}$	0.0000	0.4192	0.0000	−0.4192		(3, 1) (2, 3)
$S^{1,2}_{\sigma\varepsilon}$	0.0000	0.2420	0.0000	−0.2420		(1, 3) (2, 3) (3, 1) (3, 2) (2, 1)
$S^{1,2}_{\eta\xi}$	0.1623	−0.0270	0.2706	−0.4059	(1, 3) (2, 1)	(3, 1) (2, 3)
$S^{1,2}_{\xi\eta}$	−0.1623	0.0270	−0.2706	0.4059	(1, 3) (2, 1)	(3, 1) (2, 3)
$S^{1,2}_{\eta\phi x}$	−0.2420	0.0000	0.2420	0.0000		(1, 3) (2, 3) (2, 1) (3, 2) (1, 3)
$S^{1,2}_{\eta\phi y}$	0.000	−0.2090	0.0000	0.2096		(2, 3) (3, 1)
$S^{1,2}_{\xi\phi x}$	−0.4192	0.0000	0.4192	0.0000		(2, 3) (3, 1)
$S^{1,2}_{\xi\phi y}$	0.0000	0.1210	0.0000	−0.1210		(2, 3) (1, 3) (2, 1) (3, 1) (3, 2)
$S^{1,2}_{\phi x\phi y}$	−0.0000	−0.0000	0.0000	0.0000	(1, 3) (2, 1)	(3, 1) (2, 3)
$S^{1,2}_{\phi y\phi x}$	−0.0000	−0.0000	−0.0000	0.0000	(1, 3) (2, 1)	(3, 1) (2, 3)
$S^{1,2}_{\phi x\phi x}$	−0.6249	0.0000	−0.3749	0.0000		(1, 3) (2, 3)
$S^{1,2}_{\phi y\phi y}$	0.0000	0.9372	0.0000	0.0625		(1, 3) (2, 3)

[a] See definitions in Eq. (7) and Table 3

a rotational matrix of the third rank. Similarly for an arbitrary f orbital on atom B, we get B_s, BP_x, BP_y, BD_{xx}, BD_{xy}, BF_x and BF_y. These projection coefficients may be obtained from comparison of the same polynomial terms of R in a detailed expansion below.

$$f_A = \sum_{i,j,k} C_{ijk} \vec{A}_i \vec{A}_j \vec{A}_k = \sum_{ijk} C_{ijk} \left(\sum_l P_{il} \vec{R}_l \right) \left(\sum_m P_{jm} \vec{R}_m \right) \left(\sum_n P_{kn} \vec{R}_n \right). \tag{4}$$

For example:

$$\begin{aligned}
A_s &= \frac{1}{\sqrt{7}} \sum_{ijk} C_{ijk} P_{i3} P_{j3} P_{k3}, \\
AP_x &= \frac{1}{4} \sqrt{\frac{8}{21}} \sum_{ijk} C_{ijk} (P_{i1} P_{j3} P_{k3} + P_{i3} P_{j1} P_{k3} + P_{i3} P_{j3} P_{k1}), \\
AP_y &= \frac{1}{4} \sqrt{\frac{8}{21}} \sum_{ijk} C_{ijk} (P_{i2} P_{j3} P_{k3} + P_{i3} P_{j2} P_{k3} + P_{i3} P_{j3} P_{k2}), \\
AD_{xx} &= -\frac{4}{\sqrt{105}} \left(\frac{3\sqrt{7}}{2} A_s + \sum_{ijk} C_{ijk} (P_{i3} P_{j2} P_{k2} + P_{i2} P_{j3} P_{k2} + P_{i2} P_{j2} P_{k3}) \right), \\
AD_{xy} &= \frac{1}{\sqrt{105}} \sum_{ijk} C_{ijk} (P_{i1} P_{j2} P_{k3} + P_{i2} P_{j3} P_{k1} + P_{i3} P_{j1} P_{k2} + P_{i1} P_{j3} P_{k2} + P_{i3} P_{j2} P_{k1} \\
&\quad + P_{i2} P_{j1} P_{k3}), \\
AF_x &= \sqrt{\frac{8}{35}} \left\{ \sqrt{\frac{21}{8}} AP_x + \sum_{ijk} C_{ijk} P_{i1} P_{j1} P_{k1} \right\}, \\
AF_Y &= -\sqrt{\frac{8}{35}} \left\{ \sqrt{\frac{21}{8}} AP_y + \sum_{ijk} C_{ijk} P_{i2} P_{j2} P_{k2} \right\}.
\end{aligned} \tag{5}$$

Table 9. Atomic f-overlap between $M_3(D_{3h})$ cluster orbitals[a]

					Equivalent to	
$S^{i,j}_{k1}$	F_{SG}	F_{PI}	F_{DL}	F_F	$S_{1,k}$	$S_{k,1}$
$S^{1,2}_{\sigma\sigma}$	0.03125	0.42190	0.46878	0.07813		(1, 4) (2, 3) (3. 4)
$S^{1,3}_{\sigma\sigma}$	1.00000	0.00000	0.00000	0.00000		(2, 4)
$S^{1,3}_{\eta\eta}$	0.00000	−1.00000	0.00000	0.00000		$S^{2,4}_{\xi\xi}$
$S^{1,3}_{\xi\xi}$	0.00000	+1.00000	0.00000	0.00000		$S^{2,4}_{\eta\eta}$
$S^{1,2}_{\eta\xi}$	0.42190	0.38283	0.07813	0.11720	(2, 3)	(1, 4) (3, 4)
$S^{1,2}_{\xi\eta}$	0.00000	0.14063	0.62502	0.23437	(2, 3)	(1, 4) (3, 4)
$S^{1,2}_{\zeta\zeta}$	0.00000	0.62502	0.00000	0.37501		(1, 4) (2, 3) (3, 4)
$S^{1,2}_{\varepsilon\varepsilon}$	−0.46878	−0.07813	−0.03125	−0.42190		(1, 4) (2, 3) (3, 4)
$S^{1,3}_{\zeta\zeta}$	0.00000	0.00000	−1.00000	0.00000		(2, 4)
$S^{1,3}_{\varepsilon\varepsilon}$	0.00000	0.00000	1.00000	0.00000		(2, 4)
$S^{1,2}_{\phi x \phi y}$	−0.07813	−0.11719	−0.42190	−0.38283	(2, 3) (3, 2)	(1, 4) (3, 4)
$S^{1,2}_{\phi y \phi x}$	0.00000	−0.23438	−0.37501	−0.39062	(2, 3) (3, 2)	(1, 4) (3, 4)
$S^{1,3}_{\phi x \phi x}$	0.00000	0.00000	0.00000	−1.00000		$S^{2,4}_{\phi y \phi y}$
$S^{1,3}_{\phi y \phi y}$	0.00000	0.00000	0.00000	1.00000		$S^{2,4}_{\phi x \phi x}$

[a] See definition in Eq. (7) and Table 4

Instead of in terms of Cartesian direction cosines as above, these coefficients are also expressible in terms of rotation matrices (Eq. (9) below).

The total overlap $S(f_A f_B)$ may then be expressed in terms of the products of these coefficients and known values of overlaps integrals in tables [21, 22, 23] viz.

Sigma overlaps $S(f\sigma, f\sigma)$, *Pi* overlaps $S(f\pi, f\pi)$, delta overlap $S(f\delta, f\delta)$ and phi overlap $S(f\phi, f\phi)$ as follows:

$$\begin{aligned} S(f_A f_B) = & -\mathrm{A}_s \mathrm{B}_s S(f\sigma, f\sigma) + (\mathrm{A}P_x \mathrm{B}P_x + \mathrm{A}P_y \mathrm{B}P_Y) S(f\pi, f\pi) \\ & - (\mathrm{A}D_{xx} \mathrm{B}D_{xx} + \mathrm{A}D_{xy} \mathrm{B}D_{xy}) S(f\delta, f\delta) \\ & + (\mathrm{A}F_x \mathrm{B}F_x + \mathrm{A}F_y \mathrm{B}F_y) S(f\phi, f\phi). \end{aligned} \tag{6}$$

where the products of coefficients for decomposition into σ, π, δ and ϕ are respectively (see Tables 8–11).

$$\begin{aligned} F_{SG} &= -\mathrm{A}_s \cdot \mathrm{B}_s, \\ F_{P1} &= (\mathrm{A}P_x \cdot \mathrm{B}P_x + \mathrm{A}P_y \cdot \mathrm{B}P_y), \\ F_{DL} &= -(\mathrm{A}D_{xx} \cdot \mathrm{B}D_{xx} + \mathrm{A}D_{xy} \cdot \mathrm{B}D_{xy}), \\ F_F &= (\mathrm{A}F_x \cdot \mathrm{B}F_x + \mathrm{A}F_y \cdot \mathrm{B}F_y). \end{aligned} \tag{7}$$

These are of course, functions of rotational matrix products (see Eq. (9) below).

These coefficients are tabulated for pairs of atoms in various clusters. Many overlaps are seen to be equivalent. Such equivalence will simplify the normalization of cluster molecular orbitals as well as simplify energy expressions for symmetry-adapted orbital.

3. Discussion of results

To check the vector-method result, to see its physical meaning and to appreciate the complexity of the Euler angle method, we consider the $f\sigma - f\sigma$ overlap between atoms #1 and #2 in the $\mathrm{M}_6(O_h)$ case (Fig. 1c). The two *f*-orbitals are by Eq. (3) ($\nu = 0$)

$$\begin{aligned} f\sigma_A &= \frac{\sqrt{7}}{2} z_A(5z_A^2 - 3r_A^2) = \sqrt{4\pi}\, r_A^3 Y_3^0(\Theta_A \Phi_A) \\ &= \sqrt{4\pi} \sum_\mu D_{u0}^3(\alpha_A \beta_A \gamma_A) r_A^3 Y_3^\mu(\Theta\Phi), \end{aligned} \tag{8a}$$

$$\begin{aligned} f\sigma_B &= \frac{\sqrt{7}}{2} z_B(5z_B^2 - 3r_B^2) = \sqrt{4\pi}\, r_B^3 Y_3^0(\Theta_B \Phi_B) \\ &= \sqrt{4\pi} \sum_\mu D_{\mu 0}^3(\alpha_B \beta_B \gamma_B) r_B^3 Y_3^\mu(\Theta\Phi). \end{aligned} \tag{8b}$$

Table 10. Atomic *f*-overlap between $M_6(O_h)$ cluster orbitals[a]

					Equivalent to	
$S^{i,j}_{k1}$	F_{SG}	F_{PI}	F_{DL}	F_F	S_{1k}	S_{k1}
$S^{1,5}_{\phi x \phi x}$	0.00000	−0.23438	−0.37501	−0.39062	−(3, 5) − (3, 6)	(1, 6)
$S^{1,5}_{\phi y \phi y}$	0.07813	0.11719	0.42188	0.38283	−(3, 5) − (3, 6)	(1, 6)
$S^{5,6}_{\phi x \phi x}$	0.00000	0.00000	0.00000	1.00000	$-S^{5,6}_{\phi y \phi y}$	−(1, 3) (2, 4)
$S^{5,6}_{\phi y \phi y}$	0.00000	0.00000	0.00000	−1.00000	$-S^{5,6}_{\phi x \phi x}$	−(1, 3) (2, 4)
$S^{1,5}_{\sigma x \sigma x}$	0.03125	0.42190	0.46876	0.07813	(1, 2) (1, 4) (2, 3) (3, 4)	(1, 6) (3, 5) (3, 6) (2, 5) (2, 6) (4, 5) (4, 6)
$S^{5,6}_{\sigma y \sigma y}$	1.00000	0.00000	0.00000	0.00000	(1, 3) (2, 4)	
$S^{2,5}_{\phi x \phi x}$	0.07813	0.11719	0.42188	0.38283	−(2, 6) − (4, 5)	(4, 6)
$S^{2,5}_{\phi y \phi y}$	−0.00000	−0.23438	−0.37501	−0.39062	−(2, 6) − (4, 5)	(4, 6)
$S^{1,5}_{\xi\xi}$	0.42190	0.38283	0.07813	0.11720	−(3, 5) − (3, 6)	(1, 6)
$S^{5,6}_{\xi\xi}$	0.00000	−1.00000	0.00000	0.00000	−(1, 3)	(2, 4)
$S^{1,5}_{\eta\eta}$	0.00000	−0.14063	−0.62502	−0.23437	−(3, 5) − (3, 6)	(1, 6)
$S^{5,6}_{\eta\eta}$	0.00000	1.00000	0.00000	0.00000	−(1, 3)	(2, 4)
$S^{1,5}_{\varepsilon\varepsilon}$	0.46878	0.07813	0.03125	0.42190	−(1, 2) − (1, 4) −(2, 3) − (3, 4)	(1, 6) (3, 5) (3, 6) (2, 5) (2, 6) (4, 5) (4, 6)
$S^{5,6}_{\varepsilon\varepsilon}$	0.00000	0.00000	1.00000	0.00000		(1, 3) (2, 4)
$S^{1,5}_{\zeta\zeta}$	0.00000	−0.62502	0.00000	−0.37501	−(1, 2) − (1, 4) −(2, 3) − (3, 4)	(1, 6) (3, 5) (3, 6) (2, 5) (2, 6) (4, 5) (4, 6)
$S^{5,6}_{\zeta\zeta}$	0.00000	0.00000	−1.00000	0.00000		(1, 3) (2, 4)
$S^{1,2}_{\xi\xi}$	0.00000	0.00000	0.00000	0.00000	$S^{1,2}_{\eta\eta} S^{1,4}_{\eta\eta}$	(1, 4) (2, 3) (3, 4)
$S^{1,2}_{\sigma\varepsilon}$	0.12104	0.18156	−0.12104	−0.18156	−(4, 5) − (4, 6) (3, 5) (3, 6) −(1, 2) (2, 3) −(1, 4) − (3, 4) (1, 5) (1, 6) (2, 3) − (2, 5) −(2, 6) − (3, 4)	(1, 4) (3, 4) −(2, 3) (3, 5) (1, 5) (1, 6) −(2, 5) −(2, 6) (3, 6) −(4, 5) − (4, 6)
$S^{2,3}_{\sigma\eta}$	−0.11483	0.40189	−0.19138	−0.09569	−(1, 2) (1, 4) (2, 5) −(2, 6) − (3, 4) (4, 5) − (4, 6)	(2, 5) (2, 6) (4, 6) − (4, 5)
$S^{2,3}_{\sigma\phi x}$	−0.04941	−0.22236	0.44470	−0.17295	−(1, 2) (1, 4) (2, 5) −(2, 6) − (3, 4) (4, 5) − (4, 6)	(2, 5) (2, 6) −(4, 5) − (4, 6)
$S^{1,2}_{\eta\varepsilon}$	0.44472	−0.17295	−0.04941	−0.22236	−(2, 3) (2, 5) (2, 6) − (4, 5) −(4, 6)	−(1, 4) (2, 5) −(2, 6) (3, 4) (4, 5) − (4, 6)

Table 10 (continued)

					Equivalent to	
$S^{i,j}_{k1}$	F_{SG}	F_{PI}	F_{DL}	F_F	S_{1k}	S_{k1}
$S^{2,3}_{\varepsilon\phi x}$	−0.19138	−0.09569	−0.11482	−0.40189	−(1, 2) (1, 4) −(2, 5) (2, 6) −(3, 4) − (4, 5) (4, 6)	−(2, 5) − (2, 6) (4, 5) (4, 6)
$S^{1,2}_{\eta\phi y}$	−0.18156	0.21182	0.18156	−0.21182	−(2, 3)	(1, 4) (3, 4)
$S^{1,2}_{\phi x\xi}$	0.18156	−0.21182	−0.18156	0.21182	(2, 3)	(1, 4) (3, 4)
$S^{1,2}_{\xi\phi x}$	0.00000	−0.18155	0.48414	−0.30257	(2, 3)	(1, 4) (3, 4)
$S^{2,3}_{\eta\phi y}$	0.00000	0.18155	−0.48414	0.30257	(1, 2) (1, 4) (3, 4)	
$S^{2,3}_{\eta\zeta}$	0.00000	0.29647	0.00000	−0.29647	−(1, 2) (1, 4) − (1, 5) (1, 6) − (3, 4) (3, 5) − (3, 6)	(1, 6) (3, 6) −(1, 5) − (3, 5)
$S^{1,2}_{\zeta\phi x}$	0.00000	0.38275	0.00000	−0.38275	(1, 5) − (1, 6) −(2, 3) (3, 5) −(3, 6)	−(1, 4) (1, 5) −(1, 6) (3, 4) −(3, 5) (3, 6)

[a] See definition in Eq. (7) and Table 6

Table 11. Group *f*-orbital overlap for mixing of $M_4(D_{4h})$ cluster orbitals of the same irreducible representation[a]

Mixing of	
σ, δ	$S[B_{1g}(\sigma)B_{1g}(\varepsilon)] = 8NN'S^{1,2}_{\sigma\varepsilon}$
σ, π, δ, ϕ	$S[E_u(\sigma)E_u(\eta)] = 4NN'S^{2,3}_{\sigma\eta}$ $S[E_u(\eta)E_u(\phi_x)] = 0$ $S[E_u(\sigma)E_u(\varepsilon)] = 0$ $S[E_u(\sigma)E_u(\phi_x)] = 4NN'S^{2,3}_{\sigma\phi x}$ $S[E_u(\eta)E_u(\varepsilon)] = 4NN'S^{1,2}_{\eta\varepsilon}$ $S[E_u(\varepsilon)E_u(\phi_x)] = 4NN'S^{2,3}_{\varepsilon\phi x}$
π, ϕ	$S[B_{2g}(\pi)B_{2g}(\phi)] = 8NN'S^{2,3}_{\xi\phi x}$ $S[A_{2g}(\pi)A_{2g}(\phi)] = -8NN'S^{2,3}_{\xi\phi x}$ $S[A_{2u}(\pi)A_{2u}(\phi)] = 8NN'S^{2,3}_{\eta\phi y}$ $S[B_{2u}(\pi)B_{2u}(\phi)] = -8NN'S^{2,3}_{\eta\phi y}$
π, δ, ϕ	$S[E_g(\pi)E_g(\delta)] = 4NN'S^{2,3}_{\eta\zeta}$ $S[E_g(\pi)E_g(\phi)] = 0$ $S[E_g(\delta)E_g(\phi)] = -4NN'S^{1,2}_{\zeta\phi x}$

[a] N and N' symbolically stand for the normalization constants of the two symmetry adapted orbitals for which the group overlap is computed. Overlaps of only one-pair of corresponding components of the degenerate representations are considered

Table 12. Atomic *f*-overlaps between $M_8(O_h)$ cluster atomic orbitals[a]

$S^{i,j}_{kl}$	F_{SG}	F_{PI}	F_{DL}	F_F	Equivalent to $S_{l,k}$	$S_{k,l}$
$S^{1,2}_{\sigma\sigma}$	0.01852	0.68057	0.27779	0.02315	(5, 6) (5, 7) (5, 8) (6, 7) (6, 8) (7, 8)	(1, 3) (1, 4) (2, 3) (2, 4) (3, 4)
$S^{1,6}_{\sigma\sigma}$	0.14814	0.11111	0.55555	0.18517	(3, 6) (3, 8) (4, 5) (4, 6) (4, 7)	(1, 7) (1, 8) (2, 5) (2, 7) (2, 8) (3, 5)
$S^{2,6}_{\sigma\sigma}$	1.00000	0.00000	0.00000	0.00000	(4, 8) (7, 3)	(1, 5)
$S^{1,8}_{\xi\xi}$	0.11111	0.74998	0.00000	0.13888	(3, 6) (4, 5)	(2, 7)
$S^{1,2}_{\xi\xi}$	0.17015	−0.24480	−0.36460	−0.06076	(5, 6) (5, 7) (6, 8) (7, 8)	(1, 3) (2, 4) (3, 4)
$S^{1,4}_{\xi\xi}$	0.68057	0.04166	0.20834	0.06945	(5, 8) (6, 7)	(2, 3)
$S^{1,5}_{\xi\xi}$	0.00000	−1.00000	0.00000	0.00000	(4, 8) (3, 7)	(2, 6)
$S^{1,6}_{\xi\xi}$	0.02778	0.20832	0.41666	0.34722	(3, 8) (4, 6) (4, 7)	(1, 7) (2, 5) (2, 8) (3, 5)
$S^{1,2}_{\eta\eta}$	0.51044	−0.05382	0.01735	0.02605	(5, 6) (5, 7) (6, 8) (7, 8)	(1, 3) (2, 4) (3, 4)
$S^{1,8}_{\eta\eta}$	0.00000	−0.02778	−0.55554	−0.41668	(3, 6) (4, 5)	(2, 7)
$S^{1,4}_{\eta\eta}$	0.00000	−0.34029	−0.55554	−0.10416	(5, 8) (6, 7)	(2, 3)
$S^{1,5}_{\eta\eta}$	0.00000	1.00000	0.00000	0.00000	(7, 3) (4, 8)	(2, 6)
$S^{1,6}_{\eta\eta}$	−0.08334	−0.56942	−0.13888	−0.20833	(3, 8) (4, 6) (4, 7)	(1, 7) (2, 5) (2, 8) (3, 5)
$S^{1,2}_{\varepsilon\varepsilon}$	0.06944	−0.36459	−0.04166	−0.16320	(5, 6) (5, 7) (6, 8) (7, 8)	(1, 3) (2, 4) (3, 4)
$S^{1,4}_{\varepsilon\varepsilon}$	0.27777	0.20833	0.16668	0.34721	(5, 8) (6, 7)	(2, 3)
$S^{1,5}_{\varepsilon\varepsilon}$	0.00000	0.00000	1.00000	0.00000	(7, 3) (4, 8)	(2, 6)
$S^{1,6}_{\varepsilon\varepsilon}$	0.13889	0.41664	0.08332	0.36110	(3, 8) (4, 6) (4, 7)	(1, 7) (2, 5) (2, 8) (3, 5)
$S^{1,8}_{\varepsilon\varepsilon}$	0.55554	0.00000	0.00000	0.44443	(3, 6) (4, 5)	(2, 7)
$S^{1,2}_{\zeta\zeta}$	0.20834	0.01736	0.09722	0.17706	(5, 6) (5, 7) (6, 8) (7, 8)	(1, 3) (2, 4) (3, 4)
$S^{1,4}_{\zeta\zeta}$	0.00000	−0.55554	−0.11111	−0.33333	(3, 6) (4, 5) (5, 8) (6, 7)	(1, 8) (2, 3) (2, 7)
$S^{1,5}_{\zeta\zeta}$	0.00000	0.00000	−1.00000	0.00000	(3, 7)	(2, 6)
$S^{1,6}_{\zeta\zeta}$	−0.41664	−0.13888	−0.02778	−0.41664	(3, 8) (4, 6) (4, 7)	(1, 7) (2, 5) (2, 8) (3, 5)
$S^{1,2}_{\phi x\phi x}$	0.00000	−0.10417	−0.33333	−0.56249	(5, 6) (5, 7) (5, 8) (6, 7) (6, 8) (7, 8)	(1, 3) (1, 4) (2, 3) (2, 4) (3, 4)
$S^{1,5}_{\phi x\phi x}$	0.00000	−0.00000	0.00000	1.00000	(3, 7) (4, 8)	(2, 6)
$S^{1,6}_{\phi x\phi x}$	0.00000	−0.41664	−0.33332	−0.24999	(3, 6) (3, 8) (4, 5) (4, 6) (4, 7)	(1, 7) (1, 8) (2, 5) (2, 7) (2, 8) (3, 5)
$S^{1,2}_{\phi y\phi y}$	0.02315	0.06944	0.34721	0.56015	(5, 6) (5, 7) (5, 8) (6, 7) (6, 8) (7, 8)	(1, 3) (1, 4) (2, 3) (2, 4) (3, 4)
$S^{1,5}_{\phi y\phi y}$	0.00000	0.00000	0.00000	−1.00000	(3, 7) (4, 8)	(2, 6)
$S^{1,6}_{\phi y\phi y}$	0.18517	0.13888	0.44442	0.23147	(3, 6) (3, 8) (4, 5) (4, 6) (4, 7)	(1, 7) (1, 8) (2, 5) (2, 7) (2, 8) (3, 5)

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[a] $S^{i,j}_{\phi x\phi x}$ and $S^{i,j}_{\phi y\phi y}$ also abbreviated as $S^{i,j}_{xx}$ and $S^{i,j}_{yy}$ respectively (see Table 7 etc). Note that when the coefficients F_{SG} etc. sum to ± or 0, this indicates that the Euler angles for transformation of local A and B axes are simply related and orthonormality of the rotation matrices holds

Where for example,

$$r^3 Y_3^0(\Theta\Phi) = \frac{1}{\sqrt{4\pi}} \frac{\sqrt{7}}{2} (5R_3^3 - 3R^2 R_3)$$

$$= \frac{1}{\sqrt{4\pi}} \frac{\sqrt{7}}{2} (2R_3^3 - 3R_3 R_2^2 - 3R_3 R_1^2). \tag{8c}$$

Referring to Fig. 2, we see that the Euler angles for transformation from $\vec{R}_1 \vec{R}_2 \vec{R}_3$ to $x_1 y_1 z_1$ are $\alpha_A = \pi/2$, $\beta_A = 3\pi/4$ and $\gamma_A = \pi$. Similarly from $\vec{R}_1 \vec{R}_2 \vec{R}_3$ to $x_2 y_2 z_2$ the Euler angles are $\alpha_B = \pi/2$, $\beta_B = \pi/4$ and $\gamma_B = \pi$. From these the values of the rotation matrices may be computed. These values are substituted into the coefficients for σ, π, δ and ϕ projection (Eq. 3) for the $f\sigma$ orbitals at A (atom #1) or B (atom #2), $\nu = 0$

$$\begin{aligned}
&\mathrm{A}_s \text{ or } \mathrm{B}_s \approx D_{0\nu}^3 = && 0.17678 && \text{or} && -0.17678 \\
&\mathrm{A}P_x \text{ or } \mathrm{B}P_x = -\frac{1}{\sqrt{2}} (D_{1\nu}^3 - D_{-1\nu}^3) = 0 && && \text{or} && 0 \\
&\mathrm{A}P_y \text{ or } \mathrm{B}P_y = \frac{1}{\mathrm{i}\sqrt{2}} (D_{1\nu}^3 + D_{-1\nu}^3) = && 0.64954 && \text{or} && 0.64954 \\
&\mathrm{A}D_{xx} \text{ or } \mathrm{B}D_{xx} = \frac{1}{\sqrt{2}} (D_{2\nu}^3 + D_{-2\nu}^3) \approx && 0.68465 && \text{or} && -0.68465 \\
&\mathrm{A}D_{xy} \text{ or } \mathrm{B}D_{xy} = \frac{\mathrm{i}}{\sqrt{2}} (D_{2\nu}^3 - D_{-2\nu}^3) = 0 && && \text{or} && 0 \\
&\mathrm{A}F_x \text{ or } \mathrm{B}F_x = -\frac{1}{\sqrt{2}} (D_{3\nu}^3 - D_{-3\nu}^3) = 0 && && \text{or} && 0 \\
&\mathrm{A}F_y \text{ or } \mathrm{B}F_y = \frac{1}{\mathrm{i}\sqrt{2}} (D_{3\nu}^3 + D_{3\nu}^3) = && -0.27952 && \text{or} && -0.27952.
\end{aligned} \tag{9}$$

The explicit definitions of spherical harmonics used here may be obtained from Ballhausen's book [27] and Watanabe's [11].

Subsequent products of their projections yield the products of coefficients (Eq. (7)) for decomposition of overlap integrals that agree with the computer results (Table 10). Note that in the use of overlap integrals $S(f\sigma, f\sigma)$ etc. that occur in Eq. (6), care must be exercised to correct for the constant coefficients in the definition of the *f*-orbitals. Our definition in Eq. (1) agrees with those of Coulson and Lester [21] but differs from Boudreaux et al. [23].

From Table 2, it can be seen that the irreducible representations for *f*-orbitals are not unique. For example, there are four E_u's in $\mathrm{M}_4(D_{4h})$. One each from $f\sigma$, $f\pi$, $f\delta$ and $f\phi$. Mixing among these symmetry-adapted orbitals are possible and the energy is valid only after mixing and solution of the 4 × 4 secular determinant. The matrix elements of mixing are given (Table 11) and the necessary atomic

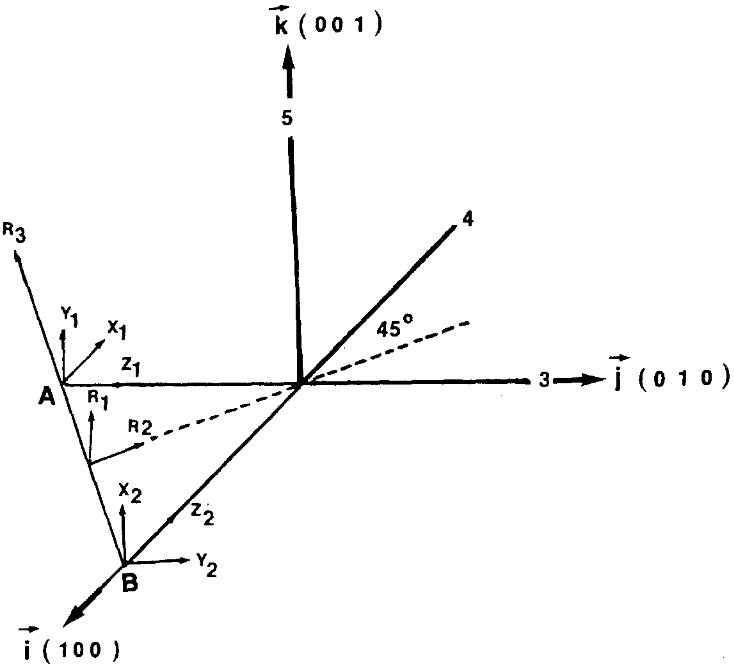

Fig. 2. The relationship between the local axes of $M_6(O_h)$ at atoms No. 1 and No. 2 and the interatomic vector and axes. $R_1 = (001)$; $R_2 = (-1/\sqrt{2}, 1/\sqrt{2}, 0)$; $R_3 = (-1/\sqrt{2}, -1/\sqrt{2}, 0)$. The Euler angles for rotation from $R_1R_2R_3$ *to* $x_1y_1z_1$ are $\alpha_1 = \pi/2$, $\beta_1 = 3\pi/4$, $\gamma_1 = \pi$. The Euler angles for rotation from $R_1R_2R_3$ to $x_2y_2z_2$ are $\alpha_2 = \pi/2$, $\beta_2 = \pi/4$, $\gamma_2 = \pi$

f-overlaps are available from Table 9. But the explicit mixing coefficients cannot be solved without numerical values of these matrix elements and work on these will be postponed to a later paper on application to specific systems.

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