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General Expressions for Group Overlap Integrals Involving *f*-Orbitals.

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General expressions are given which relate the group overlap integrals between a set of symmetry-related atoms and a central atom with the corresponding diatomic overlap integrals.

Introduction

It is only within the last few years that serious attempts have been made to carry out theoretical calculations on the electronic structure and spectra of complex ions. Although the methods used have varied widely in both sophistication and in their basic approach one common quantity appearing in all of them has been the overlap integral. Diatomic overlap integrals are classified according to the nodality of the interaction between the two centres. S_σ, S_π, S_δ and S_γ overlaps correspond to interactions which have, respectively, zero, one, two and three nodal planes containing the internuclear axis. For molecules which posses a fair degree of symmetry it is usual to use group theory to reduce a large secular determinant to block-diagonal form, whereupon it becomes necessary to replace the diatomic overlap integrals by group overlap integrals. The general relationships between group overlap integrals and diatomic overlap integrals have been discussed by several workers, most recently by Kettle[1] and Yeranos.[2] Both of these workers restricted themselves to a discussion of interactions involving *s*, *p* and *d* atomic orbitals. In the present communication we give analagous expression for interactions involving *f*-orbitals.

Results and Discussion

The forms of the real *f*-orbitals have been discussed recently by Friedman, Choppin and Feuerbacher[3] and by Becker.[4] We adopt the following definitions :

$$f_\sigma = f_{z^3} = R(r)\sqrt{7/4\pi}\,(5\cos^3\theta - 3\cos\theta)$$
$$f_\pi\,(\sigma_v \text{ sym}) = f_{xz^2} = R(r)\sqrt{42/8\pi}\,\sin\theta\,(5\cos^2\theta - 1)\cos\Phi$$
$$f_\pi\,(\sigma_v \text{ antisym}) = f_{yz^2} = R(r)\sqrt{42/8\pi}\,\sin\theta\,(5\cos^2\theta - 1)\sin\Phi$$
$$f_\delta\,(\sigma_v \text{ sym}) = f_{z(x^2-y^2)} = R(r)\sqrt{105/4\pi}\,\sin^2\theta\cos\theta\cos 2\Phi$$
$$f_\delta\,(\sigma_v \text{ antisym}) = f_{xyz} = R(r)\sqrt{105/4\pi}\,\sin^2\theta\cos\theta\sin 2\Phi$$
$$f_\gamma\,(\sigma_v \text{ sym}) = f_{x(x^2-3y^2)} = R(r)\sqrt{70/8\pi}\,\sin^3\theta\cos 3\Phi$$
$$f_\gamma\,(\sigma_v \text{ antisym}) = f_{y(3x^2-y^2)} = R(r)\sqrt{70/8\pi}\,\sin^3\theta\sin 3\Phi$$

The group overlap integral $G_n(f, \Gamma_1)$ involving a (Γ_1) symmetry—adapted linear combination of orbitals based on a set of *n* symmetry related atoms and an *f*-orbital on the central atom is given by

$$G_n(f, \Gamma_1) = \sum_j \sum_n S(\Phi_n, \theta_n, f, f_i') \, S_j \, C_n$$

where $j = \sigma, \pi, \delta$ or γ, the prime on f_j' indicating rotation of the f_j referred to the molecular axes (z along $\theta = \Phi = 0$) to those appropriate to z′ along θ_n, Φ_n. C_n is the coefficient with which the *n*th ligand orbital appears in the symmetry adapted group orbital. The coefficients $S(\theta_n, \Phi_n, f, f_i')$ are readily determined. As an example we give the derivation of the coefficient $S(\omega, 0, f_{z^3}, f_\sigma')$. Consider the axes shown in Figure 1. If

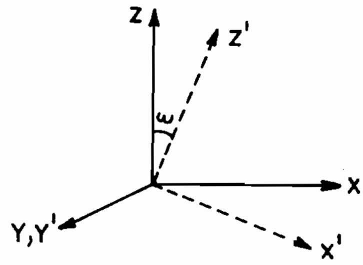

Figure 1.

the z axis is rotated by an angle ω about the y axis then the rotated axes, x′ z′ and y′ are related to the original axes x, y and thus:

$$z' = z\cos\omega + x\sin\omega$$
$$x' = x\cos\omega - z\sin\omega$$
$$y' = y$$

or, in polar coordinates

$$z' = r\cos\theta' = r(\cos\theta\cos\omega + \sin\theta\sin\omega\cos\Phi)$$
$$x' = r\sin\theta'\cos\Phi' = r(\sin\theta\cos\omega\cos\Phi - \cos\theta\sin\omega)$$
$$y' = r\sin\theta'\sin\Phi' = r\sin\theta\sin\Phi$$

(1) S. F. A. Kettle, *Inorg. Chem.*, *4*, 1821 (1965). In Table I of this paper negative signs in the expression for $G(p_x)$, $G(p_y)$, $G'(d_{xy})$ and $G'(d_{x^2-y^2})$ should be positive. The term cos Φ_n in the expression for $G(d_{yz})$ should be sin Φ_n.
(2) W. A. Yeranos, *Inorg. Chem.*, *5*, 2070 (1966).
(3) H. G. Friedman, Jr., G. R. Choppin and D. G. Feuerbaeher, *J. Chem. Educ.*, *41*, 354 (1964).
(4) L. Becker, *J. Chem. Educ.*, *41*, 358 (1964).

The *f*-orbitals defined with respect to the axes x yz can be expressed as a linear combination of *f* orbitals defined with respect to x′y′z′, for example

$$f_{z^3} = c_1 f'_{z^3} + c_2 f'_{xz^2} + c_3 f'_{(x^2-y^2)} + c_4 f'_{x(3x^2-y^2)}$$

To obtain the coefficient $S(\omega, 0, f_{z^3}, f_{\sigma}') = c_1$ we multiply by f'_{z^3} and integrate over θ and Φ after a formal integration over the radial coordinates.

$$\int_0^{\pi}\int_0^{2\pi} f'_{z^3} f_{z^3} \sin\theta\, d\theta\, d\Phi = c_1 \int_0^{\pi}\int_0^{2\pi} f'_{z^3} f_{z^3} \sin\theta\, d\theta\, d\Phi = c_1$$

That is

$$\int_0^{\pi}\int_0^{2\pi} (5\cos^3\theta - 3\cos\theta)(5\cos^3\theta' - 3\cos\theta')\sin\theta\, d\theta\, d\Phi = c_1$$

whence $c_1 = (\cos^3\omega - 3/2 \sin^2\omega \cos\omega)$.

Similarly the S_π, S_δ and S_γ coefficients can be found by evaluation of the definite integrals

$$\int_0^{\pi}\int_0^{2\pi} f_{z^3} f'_{xz^2} \sin\theta\, d\theta\, d\Phi, \quad \int_0^{\pi}\int_0^{2\pi} f_{z^3} f'_{z(x^2-y^2)} \sin\theta\, d\theta\, d\Phi$$

and

$$\int_0^{\pi}\int_0^{2\pi} f_{z^3} f_x{'}_{(3x^2-y^2)} \sin\theta\, d\theta\, d\Phi \quad \text{respectively.}$$

Table I is divided into those overlap integrals which are symmetric and antisymmetric with respect to a σ_v reflection. The molecular axes assumed are shown in Figure 2.

Table I. Group Overlap Integrals for *f*-Orbitals

(a) σ_v symmetric

$$Gf_{z^3} = \sqrt{N}\left[\cos^3\omega - \frac{3}{2}\cos\omega \sin^2\omega)S_\sigma + \frac{\sqrt{3}}{2\sqrt{2}}(5\sin^3\omega - 4\sin\omega)S_\pi + \frac{\sqrt{15}}{2}(\cos\omega - \cos^3\omega)S_\delta - \frac{\sqrt{5}}{2\sqrt{2}}\sin^3\omega\, S_\gamma\right]$$

$$Gf_{xz^2} = \left[\frac{\sqrt{3}}{2\sqrt{2}}(4\sin\omega - 5\sin^3\omega)S_\sigma + \frac{1}{4}(15\cos^3\omega - 11\cos\omega)\, S_\pi + \frac{\sqrt{5}}{2\sqrt{2}}(3\sin^3\omega - 2\sin\omega)S_\delta + \frac{\sqrt{15}}{4}(\cos\omega - \cos^3\omega)S_\gamma\right]\sum_N C_N\cos\Phi_N$$

$$Gf_{yz^2} = \left[\frac{\sqrt{3}}{2\sqrt{2}}(4\sin\omega - 5\sin^3\omega)S_\sigma + \frac{1}{4}(15\cos^3\omega - 11\cos\omega)S_\pi + \frac{\sqrt{5}}{2\sqrt{2}}(3\sin^3\omega - 2\sin\omega)S_\delta + \frac{\sqrt{15}}{4}(\cos\omega - \cos^3\omega)S_\gamma\right]\sum_N C_N\sin\Phi_N$$

$$Gf_{z(x^2-y^2)} = \left[\frac{\sqrt{15}}{2}(\cos\omega - \cos^3\omega)S_\sigma + \frac{\sqrt{5}}{2\sqrt{2}}(2\sin\omega - 3\sin^3\omega)S_\pi + \frac{1}{2}(3\cos^3\omega - \cos\omega)S_\delta + \frac{\sqrt{3}}{2\sqrt{2}}(\sin^3\omega - 2\sin\omega)S_\gamma\right]\sum_N C_N\cos2\Phi_N$$

$$Gf_{xyz} = \left[\frac{\sqrt{15}}{2}(\cos\omega - \cos^3\omega)S_\sigma + \frac{\sqrt{5}}{2\sqrt{2}}(2\sin\omega - 3\sin^3\omega)S_\pi + \frac{1}{2}(3\cos^3\omega - \cos\omega)S_\delta + \frac{\sqrt{3}}{2\sqrt{2}}(\sin^3\omega - 2\sin\omega)S_\gamma\right]\sum_N C_N\sin2\Phi_N$$

$$Gf_{x(x^2-3y^2)} = \left[\frac{\sqrt{5}}{2\sqrt{2}}\sin^3\omega S_\sigma + \frac{\sqrt{15}}{4}(\cos^3\omega - \cos\omega)S_\pi + \frac{\sqrt{3}}{2\sqrt{2}}(2\sin\omega - \sin^3\omega)S_\delta + \frac{1}{4}(\cos^3\omega + 3\cos\omega)S_\gamma\right]\sum_N C_N\cos3\Phi_N$$

$$Gf_{y(3x^2-y^2)} = \left[\frac{\sqrt{5}}{2\sqrt{2}}\sin^3\omega\, S_\sigma + \frac{\sqrt{15}}{4}(\cos^3\omega - \cos\omega)S_\pi + \frac{\sqrt{3}}{2\sqrt{2}}(2\sin\omega - \sin^3\omega)S_\delta + \frac{1}{4}(\cos^3\omega + 3\cos\omega)S_\gamma\right]\sum_N C_N\sin3\Phi_N$$

(b) σ_v antisymmetric

$$Gf_{xz^2} = \left[\frac{1}{4}(4\cos^2\omega - \sin^2\omega)S_\pi - \frac{\sqrt{5}}{\sqrt{2}}\cos\omega \sin\omega\, S_\delta + \frac{\sqrt{15}}{4}\sin^2\omega\, S_\gamma\right]\sum_N C_N\sin\Phi_N$$

$$Gf_{yz^2} = \left[\frac{1}{4}(4\cos^2\omega - \sin^2\omega)S_\pi - \frac{\sqrt{5}}{\sqrt{2}}\cos\omega \sin\omega\, S_\delta + \frac{\sqrt{15}}{4}\sin^2\omega\, S_\gamma\right]\sum_N C_N\cos\Phi_N$$

$$Gf_{z(x^2-y^2)} = \left[\frac{\sqrt{5}}{\sqrt{2}}\cos\omega \sin\omega\, S_\pi + (\cos^2\omega - \sin^2\omega)S_\delta - \frac{\sqrt{3}}{\sqrt{2}}\cos\omega \sin\omega\, S_\gamma\right]\sum_N C_N\sin2\Phi_N$$

$$Gf_{xyz} = \left[\frac{\sqrt{5}}{\sqrt{2}}\cos\omega \sin\omega\, S_\pi + (\cos^2\omega - \sin^2\omega)S_\delta - \frac{\sqrt{3}}{\sqrt{2}}\cos\omega \sin\omega\, S_\gamma\right]\sum_N C_N\cos2\Phi_N$$

$$Gf_{x(x^2-3y^2)} = \left[\frac{\sqrt{15}}{4}\sin^2\omega\, S_\pi + \frac{\sqrt{3}}{\sqrt{2}}\cos\omega \sin\omega S_\delta + \frac{1}{4}(\sin^2\omega + 4\cos^2\omega)S_\gamma\right]\sum_N C_N\sin3\Phi_N$$

$$Gf_{y(3x^2-y^2)} = \left[\frac{\sqrt{15}}{4}\sin^2\omega\, S_\pi + \frac{\sqrt{3}}{\sqrt{2}}\cos\omega \sin\omega\, S_\delta + \frac{1}{4}(\sin^2\omega + 4\cos^2\omega)S_\gamma\right]\sum_N C_N\cos3\Phi_N$$

Table II. The cubic set of *f*-orbitals

Orbital	Orbital form	L.C. of the general set
f_{z^3}	$R(r)\ \sqrt{7}/4\pi(5\cos^3\theta - 3\cos\theta)$	f_{z^3}
f_{x^3}	$R(r)\ \sqrt{7}/4\pi(\sin\theta\cos\Phi(5\sin^2\theta\cos^2\Phi - 3)$	$\frac{1}{4}(\sqrt{10}f_{x(x^2-3y^2)} - \sqrt{6}f_{xz^2})$
f_{y^3}	$R(r)\ \sqrt{7}/4\pi\ \sin\theta\sin\Phi(5\sin^2\theta\sin^2\Phi - 3)$	$-\frac{1}{4}(\sqrt{10}f_{y(3x^2-y^2)} + \sqrt{6}f_{yz^2})$
f_{xyz}	$R(r)\ \sqrt{105}/4\pi\ \sin^2\theta\cos\theta\sin 2\Phi$	f_{xyz}
$f_{z(x^2-y^2)}$	$R(r)\ \sqrt{105}/4\pi\ \sin^2\theta\cos\theta\cos 2\Phi$	$f_{z(x^2-y^2)}$
$f_{x(z^2-y^2)}$	$R(r)\ \sqrt{105}/4\pi\ \sin\theta\cos\Phi(\cos^2\theta - \sin^2\theta\sin^2\Phi)$	$\frac{1}{4}(\sqrt{10}f_{xz^2} + \sqrt{6}f_{x(x^2-3y^2)})$
$f_{y(z^2-x^2)}$	$R(r)\ \sqrt{105}/4\pi\ \sin\theta\sin\Phi(\cos^2\theta - \sin^2\theta\cos^2\Phi)$	$\frac{1}{4}(\sqrt{10}f_{yz^2} - \sqrt{6}f_{y(3x^2-y^2)})$

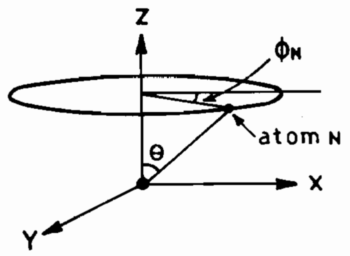

Figure 2.

For cubic point groups it is simplest to use a different set of *f*-orbitals. The inter-relation between the two sets is given, for convenience, in Table II. Using Tables I and II together it is a simple matter to derive group overlap integrals for the cubic point groups.

A compilation of overlap integrals involving *f*-orbitals has recently been published.[5] Jørgensen, Pappalardo and Schmidtke[6] have given both some σ overlap integrals appropriate to *f*-orbitals and expressions for some group overlap integrals involving them.

The involvement of *f*-orbitals in chemical bonding has been discussed by many authors.[7]

(5) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Phys.*, *46*, 2005 (1967).
(6) C. K. Jørgensen, R. Pappalardo and H. H. Schmidtke, *J. Chem. Phys*, *39*, 1422 (1963).
(7) See, for example, S. F. A. Kettle and A. J. Smith, *J. Chem. Soc.*, (A), 688 (1967), J. C. Eisenstein, *J. Chem. Phys.*, *25*, 142 (1956) and C. A. Coulson and G. R. Lester, *J. Chem. Soc.*, 3650 (1956).