Chemical Bonds involving d-*Orbitals. Part II.**

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Overlap integrals for some of the possible combinations of 3*s*-, 3*p*-, 3*d*-, 4*s*-, and 4*p*-orbitals have been evaluated for the ranges of the variables p and t which are of importance for chemical binding. Functions of Slater form have been used.

We have evaluated overlap integrals involving 3*s*-, 3*p*-, 3*d*-, and in a few cases 4*s*- and 4*p*-orbitals. Functions of Slater form have been used. The explicit expressions for typical orbitals are :

$$\psi_{3s} = \frac{2\alpha^{7/2}}{3\sqrt{10\pi}} . r^2 . e^{-\alpha r}$$

$$\psi_{3p_\sigma} = \frac{2\alpha^{7/2}}{\sqrt{30\pi}} . r^2 . \cos\theta . e^{-\alpha r}$$

$$\psi_{3p_\pi} = \frac{2\alpha^{7/2}}{\sqrt{30\pi}} . r^2 . \sin\theta . \cos\phi . e^{-\alpha r}$$

$$\psi_{3d_{z^2}} = \frac{\alpha^{7/2}}{3\sqrt{2\pi}} . r^2 (3\cos^2\theta - 1) . e^{-\alpha r}$$

$$\psi_{3d_{xz}} = \frac{\sqrt{2} . \alpha^{7/2}}{\sqrt{3\pi}} . r^2 . \sin\theta . \cos\theta . \cos\phi . e^{-\alpha r}$$

$$\psi_{4s} = \frac{\alpha^{9/2}}{3\sqrt{35\pi}} . r^3 . e^{-\alpha r}$$

$$\psi_{4p} = \frac{\alpha^{9/2}}{\sqrt{105\pi}} . r^3 . \cos\theta . e^{-\alpha r}$$

The internuclear axis is taken as the z-axis of the co-ordinate system unless otherwise stated. It should be noticed that the 4*s*- and the 4*p*-orbitals are not obtained in quite the manner suggested by Slater. If, as he suggests, ψ_{4s} is taken to be $Nr^{2.7}e^{-\alpha r}$ the evaluation of the overlap integral could not be carried out in the usual way. Instead, the nearest integral power of r has been taken.

We have used the method of evaluation described by Mulliken, Riecke, Orloff, and Orloff (*J. Chem. Phys.*, 1949, **17**, 1248).

The overlap integrals evaluated were :

σ-*Type.* $S(3s\text{–}3p)$; $S(3p\text{–}3p)$; $S(3p_z\text{–}3d_{z^2})$; $S(3p\text{–}4s)$ equicentre case only; $S(3p\text{–}4p)$ equicentre case only.

π-*Type.* $S(3d_\pi\text{–}3d_\pi)$; $S(3p_\pi\text{–}3d_\pi)$.

δ-*Type.* $S(3d_\delta\text{–}3d_\delta)$.

σ-*Symbatic Type.* $S(3d_{z^2}\text{–}3d_{z^2})$.

Diagrams of the less familiar bond types considered are shown in Part I, Fig. 1.

The explicit expressions for the overlap integrals are :

$$S(3s\text{–}3p) = \frac{\sqrt{3}(1-t^2)^{7/2}p^7}{1440}[A_0B_5 + A_1(B_4 - B_6) - A_2(2B_3 + B_5) - 2A_3(B_2 - B_4) + A_4(B_1 + 2B_3) + A_5(B_0 - B_2) - A_6B_1]$$

$$S(3p_\sigma\text{–}3p_\sigma) = \frac{(1-t^2)^{7/2}p^7}{480}[A_0B_4 - A_2(2B_2 + B_6) + A_4(B_0 + 2B_4) - A_6B_2]$$

* Part I, preceding paper.

$$S(3p_z\text{–}3d_{z^2}) = \frac{(1-t^2)^{7/2}p^7}{64\sqrt{15}}[A_0(3B_3 - B_5) + A_1(-3B_2 + 2B_4 + B_6) - A_2(3B_1 + B_3 + 2B_5) + A_3(3B_0 - B_2 + B_4 - 3B_6) + A_4(2B_1 + B_3 + 3B_5) + A_5(-B_0 - 2B_2 + 3B_4) + A_6(B_1 - B_3)]$$

$$S(3p_\pi\text{–}3d_\pi) = \frac{\sqrt{5}(1-t^2)^{7/2}p^7}{960}[A_0(B_3 - B_5) + A_1(B_2 - 2B_4 + B_6) + A_2(-B_1 - B_3 + 2B_5) + A_3(-B_0 + B_2 + B_4 - B_6) + A_4(2B_1 - B_3 - B_5) + A_5(B_0 - 2B_2 + B_4) + A_6(-B_1 + B_3)]$$

$$S(3d_\pi\text{–}3d_\pi) = \frac{(1-t^2)^{7/2}p^7}{192}[A_0(B_2 - B_4) + A_2(-B_0 + B_6) + A_4(B_0 - B_6) + A_6(-B_2 + B_4)]$$

$$S(3d_\delta\text{–}3d_\delta) = \frac{(1-t^2)^{7/2}p^7}{768}[A_0(-B_2 + 2B_4 - B_6) + A_2(B_0 - 3B_4 + 2B_6) + A_4(-2B_0 + 3B_2 - B_6) + A_6(B_0 - 2B_2 + B_4)]$$

$$S(3d_{z^2}\text{–}3d_{z^2}) = \frac{(1-t^2)^{7/2}p^7}{9216}[A_0(-27B_2 + 30B_4 - 11B_6) + A_2(27B_0 - 33B_4 + 30B_6) + A_4(-30B_0 + 33B_2 - 27B_6) + A_6(11B_0 - 30B_2 + 27B_4)]$$

$$S(3p\text{–}4s)\text{ equicentre} = \frac{p^8}{50{,}400\sqrt{42}}(15A_0 - 51A_2 + 49A_4 + 35A_6)$$

$$S(3p\text{–}4p)\text{ equicentre} = \frac{p^8}{50{,}400\sqrt{14}}(21A_1 - 85A_3 + 147A_5 - 35A_7)$$

The numerical evaluation of a large number of overlap integrals can now be attempted in two ways. Either the incomplete Γ-functions, denoted as A_n and B_m, are expressed analytically, or numerical values are substituted immediately. We found the latter method more rapid.

Values of these functions are available in the literature (Rosen, *Phys. Review*, 1931, **38**, 255; Kotani, Amemiya, and Simose, *Proc. Phys. Mat. Soc. Jap.*, 1938, **20**, No. 1) for a wide range of arguments. However, a number of them which were not available have been calculated. If the argument is greater than one, the following recursion formulæ may be used :

$$A_n(\alpha) = \frac{1}{\alpha}\{e^{-\alpha} + nA_{n-1}(\alpha)\}$$

$$B_m(\alpha) = \frac{1}{\alpha}\{(-1)^m e^{\alpha} - e^{-\alpha} + mB_{m-1}(\alpha)\}$$

For small values of the argument, the functions B_m can easily be computed by means of a power series expansion.

For tabulation we have found it convenient to use the independent variables t and p introduced by Mulliken *et al.* (*loc. cit.*) in their paper on *s*- and *p*-orbital overlap integrals. These variables are defined as :

$$t = (\alpha_A - \alpha_B)/(\alpha_A + \alpha_B) \text{ and } p = \tfrac{1}{2}(\alpha_A + \alpha_B)\rho$$

where α_A and α_B are the exponents appropriate to the bonding orbitals and ρ is the internuclear distance in Å. It should be noted that t measures the asymmetry of the bond.

Overlap integrals between hybridised orbitals are obtained in the usual way (Mulliken *et al.*, *loc. cit.*), *i.e.*, if $\psi_A = \sum_i c_i\phi_i$ then $S_{AB} = \sum_i c_i S_{iB}$. Values of the overlap integrals are given in Tables 1—8. Some useful values of the B-functions are given in Table 9. Overlap values for some hybrid orbitals are shown in Figs. 2*A*, 2*B*, 4*A*, 4*B*, 7*A*, and 7*B* of Part I.

TABLE 1. *Overlap integrals:* $S(3s\text{–}3p)$.

p/t	−0·5	−0·4	−0·3	−0·2	−0·1	0·0	0·1	0·2	0·3	0·4	0·5
2	−0·035	0·001	0·067	0·157	0·257	0·354	0·427	0·466	0·459	0·407	0·318
3	−0·012	0·046	0·134	0·244	0·361	0·468	0·550	0·593	0·587	0·529	0·426
4	0·025	0·098	0·194	0·303	0·413	0·551	0·586	0·628	0·629	0·581	0·484
5	0·061	0·136	0·225	0·318	0·405	0·483	0·544	0·585	0·596	0·568	0·496
6	0·083	0·152	0·223	0·291	0·353	0·408	0·455	0·493	0·514	0·551	0·469
7	0·093	0·148	0·198	0·241	0·279	0·314	0·349	0·383	0·412	0·429	0·417
8	0·092	0·130	0·160	0·184	0·204	0·225	0·249	0·279	0·312	0·341	0·354
9	0·083	0·107	0·122	0·131	0·140	0·151	0·168	0·192	0·224	0·259	0·288
10	0·071	0·083	0·085	0·088	0·091	0·096	0·107	0·126	0·155	0·190	0·227

TABLE 2. *Overlap integrals:* $S(3p_\sigma\text{–}3p_\sigma)$.

p/t	0	0·1	0·2	0·3	0·4	0·5	p/t	0	0·1	0·2	0·3	0·4	0·5
2	−0·531	−0·520	−0·488	−0·435	−0·361	−0·272	7	0·346	0·338	0·312	0·268	0·205	0·129
3	−0·140	−0·146	−0·161	−0·178	−0·183	−0·170	8	0·273	0·269	0·257	0·233	0·194	0·138
4	0·170	0·155	0·111	0·050	−0·013	−0·060	9	0·195	0·195	0·193	0·185	0·166	0·130
5	0·342	0·324	0·275	0·200	0·114	0·033	10	0·130	0·132	0·135	0·137	0·132	0·114
6	0·385	0·371	0·331	0·266	0·184	0·096							

TABLE 3. *Overlap integrals:* $S(3p_z\text{–}3d_{z^2})$.

p/t	−0·5	−0·4	−0·3	−0·2	−0·1	0·0	0·1	0·2	0·3	0·4	0·5
2	−0·063	−0·122	−0·197	−0·279	−0·358	−0·423	−0·464	−0·473	−0·447	−0·386	−0·297
3	−0·073	−0·123	−0·178	−0·231	−0·279	−0·318	−0·347	−0·360	−0·355	−0·327	−0·272
4	−0·060	−0·082	−0·096	−0·101	−0·102	−0·105	−0·114	−0·131	−0·152	−0·170	−0·171
5	−0·033	−0·025	−0·002	0·030	0·063	0·088	0·095	0·080	0·044	−0·005	−0·053
6	−0·004	0·024	0·066	0·116	0·163	0·199	0·215	0·206	0·171	0·113	0·044
7	0·018	0·054	0·100	0·149	0·194	0·228	0·248	0·247	0·223	0·174	0·106
8	0·031	0·066	0·106	0·144	0·178	0·205	0·224	0·230	0·220	0·188	0·134
9	0·036	0·065	0·094	0·120	0·142	0·161	0·176	0·187	0·188	0·174	0·138
10	0·036	0·057	0·075	0·090	0·103	0·114	0·127	0·138	0·146	0·145	0·128

TABLE 4. *Overlap integrals:* $S(3d_\pi\text{–}3d_\pi)$.

p/t	0	0·1	0·2	0·3	0·4	0·5	p/t	0	0·1	0·2	0·3	0·4	0·5
1	−0·802	−0·776	−0·702	−0·589	−0·452	−0·311	6	0·319	0·309	0·281	0·235	0·177	0·114
2	−0·365	−0·357	−0·334	−0·297	−0·245	−0·183	7	0·245	0·240	0·223	0·195	0·156	0·109
3	0·044	0·036	0·015	−0·012	−0·037	−0·051	8	0·169	0·167	0·159	0·145	0·123	0·093
4	0·282	0·268	0·227	0·169	0·104	0·046	9	0·108	0·108	0·106	0·101	0·091	0·074
5	0·353	0·339	0·299	0·239	0·168	0·098							

TABLE 5. *Overlap integrals:* $S(3p_\pi\text{–}3d_\pi)$.

p/t	−0·5	−0·4	−0·3	−0·2	−0·1	0	0·1	0·2	0·3	0·4	0·5
1	0·028	0·064	0·114	0·173	0·232	0·282	0·312	0·317	0·293	0·245	0·182
2	0·056	0·119	0·203	0·300	0·395	0·474	0·523	0·532	0·496	0·420	0·315
3	0·078	0·153	0·248	0·353	0·455	0·539	0·592	0·604	0·571	0·492	0·380
4	0·088	0·160	0·246	0·338	0·425	0·497	0·545	0·561	0·539	0·478	0·382
5	0·086	0·146	0·214	0·282	0·345	0·399	0·437	0·456	0·449	0·412	0·345
6	0·078	0·122	0·168	0·212	0·253	0·289	0·317	0·336	0·341	0·327	0·288
7	0·065	0·094	0·123	0·148	0·172	0·193	0·231	0·213	0·242	0·244	0·227
8	0·051	0·069	0·085	0·097	0·109	0·122	0·135	0·149	0·163	0·173	0·172
9	0·039	0·049	0·056	0·061	0·066	0·073	0·081	0·092	0·106	0·119	0·127

TABLE 6. *Overlap integrals:* $S(3d_{z^2}\text{–}3d_{z^2})$.

p/t	0	0·1	0·2	0·3	0·4	0·5	p/t	0	0·1	0·2	0·3	0·4	0·5
1	0·891	0·856	0·776	0·647	0·493	0·335	6	0·130	0·127	0·119	0·106	0·089	0·069
2	0·659	0·639	0·582	0·487	0·380	0·265	7	0·097	0·094	0·088	0·079	0·066	0·052
3	0·424	0·413	0·381	0·329	0·264	0·192	8	0·071	0·069	0·066	0·059	0·051	0·041
4	0·270	0·264	0·246	0·217	0·178	0·134	9	0·050	0·049	0·047	0·044	0·038	0·031
5	0·181	0·177	0·166	0·147	0·123	0·094	10	0·034	0·033	0·033	0·029	0·028	0·024

TABLE 7. *Overlap integrals:* $S(3d_\delta\text{–}3d_\delta)$.

p/t	0	0·1	0·2	0·3	0·4	0·5	p/t	0	0·1	0·2	0·3	0·4	0·5
1	0·932	0·900	0·810	0·674	0·512	0·347	6	0·137	0·136	0·131	0·121	0·107	0·088
2	0·762	0·737	0·668	0·562	0·433	0·298	7	0·077	0·077	0·076	0·073	0·068	0·059
3	0·558	0·542	0·496	0·424	0·334	0·237	8	0·042	0·042	0·043	0·043	0·042	0·039
4	0·373	0·364	0·338	0·296	0·238	0·178	9	0·022	0·022	0·022	0·024	0·026	0·025
5	0·233	0·228	0·216	0·194	0·164	0·127	10	0·011	0·011	0·012	0·014	0·015	0·016

TABLE 8. *Overlap integrals: S(3p–4s) and S(3p–4p) equicentre case.*

p	2	3	4	5	6	7	8	9	10
$S(3p–4s)$	0·175	0·276	0·357	0·395	0·384	0·335	0·269	0·200	0·140
$S(3p–4p)$	−0·600	−0·279	0·029	0·252	0·365	0·383	0·340	0·270	0·198

TABLE 9. $B_n(\alpha) = \int_{-1}^{+1} x^n e^{-\alpha x} dx.$

α	$B_0(\alpha)$	$-B_1(\alpha)$	$B_2(\alpha)$	$-B_3(\alpha)$	$B_4(\alpha)$	$-B_5(\alpha)$	$B_6(\alpha)$	$-B_7(\alpha)$	$B_8(\alpha)$
0	2	0	0·666667	0	0·400000	0	0·285714	0	0·222222
0·1	2·00334	0·066733	0·668668	0·040048	0·401429	0·028608	0·286826	0·022252	0·223132
0·2	2·01336	0·133867	0·674686	0·080381	0·405729	0·057440	0·290171	0·044687	0·225869
0·3	2·03014	0·201806	0·684763	0·121290	0·412932	0·086718	0·295776	0·067488	0·230456
0·4	2·05376	0·270958	0·698973	0·163067	0·423095	0·116672	0·303687	0·090841	0·236933
0·5	2·08438	0·341741	0·717416	0·206011	0·436297	0·147534	0·313969	0·114939	0·245353
0·6	2·12218	0·414586	0·740224	0·250431	0·452640	0·179547	0·326706	0·139979	0·255789
0·7	2·16738	0·489937	0·767562	0·296648	0·472253	0·212961	0·342003	0·166167	0·268329
0·8	2·22026	0·568256	0·799625	0·344995	0·495288	0·248037	0·359985	0·193719	0·283079
0·9	2·28115	0·650027	0·836643	0·395825	0·521925	0·285052	0·380800	0·222861	0·300164
1·0	2·35040	0·735759	0·878885	0·449507	0·552373	0·324927	0·404618	0·253834	0·319730
1·1	2·42845	0·825988	0·926653	0·506435	0·586869	0·366083	0·431636	0·286895	0·341942
1·2	2·51577	0·921285	0·980294	0·567025	0·625685	0·410739	0·462076	0·322317	0·366989
1·3	2·61290	1·02226	1·04019	0·631726	0·669124	0·458620	0·496188	0·360394	0·395085
1·4	2·72043	1·12955	1·10679	0·701106	0·717529	0·510108	0·534254	0·401443	0·426468
1·5	2·83904	1·24385	1·18057	0·775410	0·771280	0·565613	0·576587	0·445806	0·461406

Since the completion of this work, Jaffé has published tables of some of the overlap integrals which we have calculated, but he uses different intervals for t (*J. Chem. Phys.*, 1953, **21**, 258). The only discrepancy which we have found, where comparison is possible, is that his values for the $3p_\pi$–$3d_\pi$ overlap are systematically too large and should be multiplied by 0·9736.

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