

Covalecence Reduction Factors of Four-Coordinated Pseudo-Tetrahedral Paramagnetic Compounds in D_{2d} Symmetry

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Theoretical expressions for the covalecence reduction factors of orbital angular momentum and spin-orbit coupling in pseudo-tetrahedral four-coordinated paramagnetic complexes with D_{2d} symmetry, denoted as k 's and R 's respectively, have been derived.

The mixing coefficients in the antibonding MO's for the CuCl_4^{2-} ion in three complexes are estimated using suitable approximations. It is shown that k 's must be less than R 's in Tinkham's approximation. Certain misconceptions existing in the literature regarding the value of the integral $\langle p_u | \partial / \partial u | s \rangle$ have been clarified.

Key words: Covalecence reduction factors in D_{2d} symmetry – Bonding – Mixing coefficients.

1. Introduction

Covalecence is taken care of in the derivation of expressions of epr anisotropic g 's and principal magnetic susceptibilities (K 's) by introducing reduction factors usually called orbital reduction (k) and spin orbit coupling reduction factors (R) [1, 2] and defined as

$$k = \frac{\langle \phi_i | \hat{l} | \phi_j \rangle}{\langle d_i | \hat{l} | d_j \rangle} \quad \text{and} \quad R = \frac{\langle \phi_i | \zeta \hat{l} | \phi_j \rangle}{\langle d_i | \zeta \hat{l} | d_j \rangle} \quad (1)$$

where $|\phi_i\rangle$ and $|\phi_j\rangle$ are the antibonding MO's transforming according to the same irreducible representations of the symmetry group as the corresponding d -orbitals

$|d_i\rangle$ and $|d_i\rangle$ respectively; \hat{l} and $\zeta\hat{l}$ are the one electron orbital and spin-orbit coupling operators, respectively.

Expressions of k 's and R 's have been derived for salts and complexes belonging to O_h [1, 2, 3], T_d [4], D_{4h} [5], D_{3h} and C_{4v} [6] symmetries. In this paper we derive expressions of k 's and R 's (following Tinkham's [2] and Misetich and Buch's [7] methods) in salts and complexes of D_{2d} symmetry like tetrachlorocuprate(II) [8, 9], which have been studied by epr [10], magnetic anisotropy [11] and spectral [12] methods. We also point out for the first time that $k < R$ where R is derived using Tinkham's approximation. Moreover, certain uncertainties [3] regarding the value of the integral "P" (defined in Section 3) have been clarified. Expressions of k 's and R 's derived here are used to estimate mixing coefficients occurring in MO's for some tetrachlorocuprate(II) complexes.

2. The Antibonding Molecular Orbitals

The antibonding MO's used in deriving expressions of k 's and R 's are obtained following standard group-theoretical methods [13, 14], (the orientations of the axes are as given in Fig. 1) and these are given in Eq. (2):

$$|a_1\rangle = N_{a_1} \left[d_{z^2} - \frac{\gamma}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) - \frac{\lambda}{2}(x_1 + x_2 + x_3 + x_4) \right] \quad (a)$$

$$|b_1\rangle = N_{b_1} \left[d_{x^2-y^2} - \frac{\lambda_1}{2}(y_1 + y_2 + y_3 + y_4) \right] \quad (b)$$

$$|b_2\rangle = N_{b_2} \left[d_{xy} - \frac{\gamma_2}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) - \frac{\lambda_2}{2}(x_1 + x_2 - x_3 - x_4) \right] \quad (c)$$

$$|e\rangle = \begin{cases} |e_\xi\rangle = N_{e_\xi} \left[d_{yz} - \frac{\gamma_3}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4) - \frac{\lambda_3}{2}(x_1 - x_2 - x_3 + x_4) \right. \\ \qquad \qquad \qquad \left. - \frac{\mu_3}{2}(y_1 - y_2 - y_3 + y_4) \right] & (d) \\ |e_\eta\rangle = N_{e_\eta} \left[d_{xz} - \frac{\gamma'_3}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) - \frac{\lambda'_3}{2}(x_1 - x_2 + x_3 - x_4) \right. \\ \qquad \qquad \qquad \left. - \frac{\mu'_3}{2}(y_1 - y_2 + y_3 - y_4) \right] & (e) \end{cases} \quad (2)$$

where d_{z^2} , $d_{x^2-y^2}$, ..., etc. are metal ion d -orbitals, σ_i , x_i and y_i ($i = 1, 2, 3, 4$) are hybrid sp [6], p_y and p_z orbitals respectively of ligand atom i , and γ , λ , λ_1 , ..., etc. are the mixing coefficients. Following usual convention [4, 6] we have neglected the mixing of d -orbitals with the p and s -orbitals of the central atom which are permitted by symmetry.

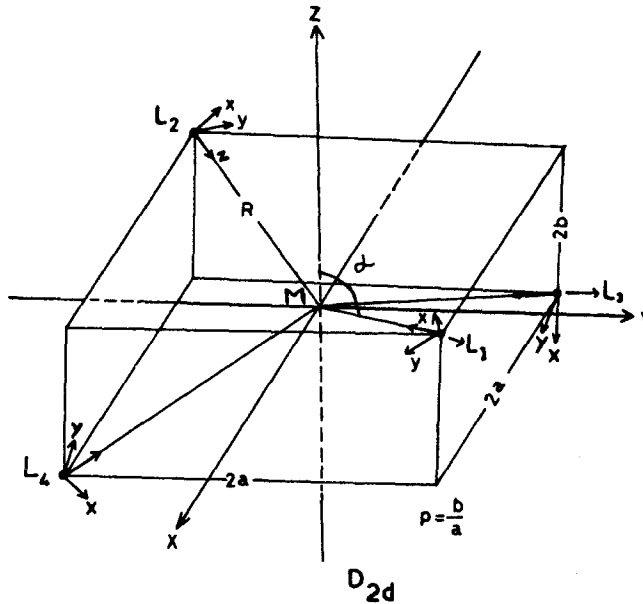


Fig. 1. The arrows at the sites L_1, L_2, L_3 and L_4 pointing to the origin of XYZ represent the ligand z axes. The axis x_1 (at site L_1) is chosen to lie in the plane passing through L_1 and the Z axis while y_1 is chosen perpendicular to this plane so that the coordinate system $x_1y_1z_1$ is left handed. The orientations of the coordinate systems at the remaining sites can be obtained by successive operations of C_{2xz}, C_{2yz} and C_{2z} on $x_1y_1z_1$. The parameter $p = b/a$ is given by $\sqrt{2} \cot \alpha$ [16]

The normalization constants for the above MO's are

$$N_{a_1} = [1 + \gamma^2 + \lambda^2 - \sqrt{2}(3E^2 - 1)\gamma(S_1 + S_2) + 4\sqrt{3}BE\lambda S_3]^{-1/2} \tag{a}$$

$$N_{b_1} = [1 + \lambda_1^2 + 4\sqrt{2}D\lambda_1 S_3]^{-1/2} \tag{b}$$

$$N_{b_2} = [1 + \gamma_2^2 + \lambda_2^2 - 2\sqrt{6}D^2\gamma_2(S_1 + S_2) - 8AD\lambda_2 S_3]^{-1/2} \tag{c} \tag{3}$$

$$N_{e_e} = [1 + \gamma_3^2 + \lambda_3^2 + \mu_3^2 - 2\sqrt{6}DE\gamma_3(S_1 + S_2) - 4(AE - BD)\lambda_3 S_3 + 2\sqrt{2}E\mu_3 S_3]^{-1/2} \tag{d}$$

$$N_{e_n} = [1 + \gamma_3'^2 + \lambda_3'^2 + \mu_3'^2 - 2\sqrt{6}DE\gamma_3'(S_1 + S_2) - 4(AE - BD)\lambda_3' S_3 + 2\sqrt{2}E\mu_3' S_3]^{-1/2} \tag{e}$$

where

$$A = \sqrt{\frac{p^2}{2p^2 + 4}}; \quad B = \sqrt{\frac{4}{2p^2 + 4}}; \quad D = \frac{1}{\sqrt{2 + p^2}}; \quad E = \frac{p}{\sqrt{2 + p^2}}$$

and S_1, S_2 and S_3 are the diatomic overlap integrals [15]

$$S_1 = \langle s_1 | d_{z^2} \rangle = S(ns_\sigma, 3d_\sigma, R); \quad S_2 = \langle z_1 | d_{z^2} \rangle = S(np_\sigma, 3d_\sigma, R);$$

$$S_3 = \langle x_1 | d_{xy} \rangle = S(np_\pi, 3d_\pi, R)$$

between a metal d -orbital and a ligand orbital and where $n = 2$ or 3 depending upon whether second or third row elements form the ligands.

3. Orbital and Spin Orbit Coupling Reduction Factors

The expressions of k 's and R 's as defined in Eqn. (1), where the antibonding MO's are given in Eq. (2), are derived for all possible cases following standard procedure [3, 6] and these are given in Eq. (4)

$$\begin{aligned}
 k_1 &= \frac{\langle a_1 | \hat{l}_x | e_\xi \rangle}{\langle d_{z^2} | \hat{l}_x | d_{yz} \rangle} = \frac{\langle a_1 | \hat{l}_y | e_\eta \rangle}{\langle d_{z^2} | \hat{l}_y | d_{xz} \rangle} \\
 &= N_{e_\xi} N_{a_1} \left[1 - \frac{\gamma(3E^2 - 1)}{\sqrt{2}} (S_1 + S_2) + \lambda(2\sqrt{3}BE)S_3 \right. \\
 &\quad - \mu_3\sqrt{2}ES_3 - \gamma_3\sqrt{6}DE(S_1 + S_2) \\
 &\quad \left. - \lambda_3 2(AE - BD)S_3 + \left(PM + \frac{1}{\sqrt{2}} \right) \frac{\{\lambda\gamma_3 - \gamma\lambda_3\}}{\sqrt{6}} + \frac{\gamma\mu_3}{\sqrt{6}} \left(\frac{pP}{\sqrt{2}} + A \right) - \frac{\lambda\mu_3 D}{\sqrt{3}} \right] \quad (a)
 \end{aligned}$$

$$\begin{aligned}
 k_2 &= \frac{\langle b_1 | \hat{l}_x | e_\xi \rangle}{\langle d_{x^2-y^2} | \hat{l}_x | d_{yz} \rangle} = \frac{\langle b_1 | \hat{l}_y | e_\eta \rangle}{\langle d_{x^2-y^2} | \hat{l}_y | d_{xz} \rangle} \\
 &= N_{e_\xi} N_{b_1} \left[1 + \lambda_1\sqrt{8}DS_3 - \gamma_3\sqrt{6}DE(S_1 + S_2) - \lambda_3 2(AE - BD)S_3 - \mu_3\sqrt{2}ES_3 \right. \\
 &\quad \left. + \frac{\lambda_1\lambda_3 B}{\sqrt{2}} - \frac{\lambda_1\gamma_3}{2} (pP + E) \right] \quad (b)
 \end{aligned}$$

$$\begin{aligned}
 k_3 &= \frac{\langle b_2 | \hat{l}_x | e_\eta \rangle}{\langle d_{xy} | \hat{l}_x | d_{xz} \rangle} = \frac{\langle b_2 | \hat{l}_y | e_\xi \rangle}{\langle d_{xy} | \hat{l}_y | d_{yz} \rangle} \quad (4) \\
 &= N_{b_2} N_{e_\xi} \left[1 - \gamma_2\sqrt{6}D^2(S_1 + S_2) - \lambda_2 4ADS_3 - \gamma_3\sqrt{6}DE(S_1 + S_2) - \mu_3\sqrt{2}ES_3 \right. \\
 &\quad - \lambda_3 2(AE - BD)S_3 + \frac{(PM + 1/\sqrt{2})}{\sqrt{2}} \{\lambda_2\gamma_3 - \gamma_2\lambda_3\} \\
 &\quad \left. - \frac{\gamma_2\mu_3}{\sqrt{2}} \left(\frac{pP}{\sqrt{2}} + A \right) + \lambda_2\mu_3 D \right] \quad (c)
 \end{aligned}$$

$$\begin{aligned}
 k_4 &= \frac{\langle b_1 | \hat{l}_z | b_2 \rangle}{\langle d_{x^2-y^2} | \hat{l}_z | d_{xy} \rangle} \\
 &= N_{b_1} N_{b_2} \left[1 + \sqrt{8}DS_3\lambda_1 - \gamma_2\sqrt{6}D^2(S_1 + S_2) \right. \\
 &\quad \left. - \lambda_2 4ADS_3 - \frac{\lambda_1\gamma_2(P + D)}{2} - \frac{\lambda_1\lambda_2 A}{\sqrt{2}} \right] \quad (d)
 \end{aligned}$$

$$\begin{aligned}
 k_5 &= \frac{\langle e_\eta | \hat{l}_z | e_\xi \rangle}{\langle d_{xz} | \hat{l}_z | d_{yz} \rangle} \\
 &= N_{e_\xi} N_{e_\eta} \left[1 - \gamma'_3 \sqrt{6} DE (S_1 + S_2) \right. \\
 &\quad - \lambda'_3 2(AE - BD) S_3 - \mu'_3 \sqrt{2} ES_3 - \gamma_3 \sqrt{6} DE (S_1 + S_2) \\
 &\quad - \lambda_3 2(AE - BD) S_3 - \mu_3 \sqrt{2} ES_3 - \mu'_3 \gamma_3 (P + D) - \mu'_3 \lambda_3 A \sqrt{2} \\
 &\quad \left. + \frac{\gamma'_3 \mu_3}{\sqrt{2}} (P + B) + \lambda'_3 \mu_3 E \right] \quad (e)
 \end{aligned}$$

where $M = \sqrt{(p^2 + 2)/2}$.

While evaluating matrix elements of \hat{l} over symmetry adapted combinations of ligand orbitals e.g. the element

$$\langle \frac{1}{2}(y_1 + y_2 + y_3 + y_4) | \hat{l}_z | \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) \rangle$$

it becomes necessary to translate \hat{l} (referred to the central metal ion coordinate system) to the respective ligand atom sites (cf. Fig. 1) so that

$$\hat{l}_z = \frac{A}{\sqrt{2}} \hat{l}_{Lz1} - \sqrt{2} D \hat{l}_{Lx1} + i\sqrt{2} \frac{\partial}{\partial y_1}$$

where \hat{l}_{Lx1} , and \hat{l}_{Lz1} are orbital angular momentum operators referred to the coordinate system at ligand atom 1 (c.f. Fig. 1). We therefore have to evaluate one-centre integrals of the form $P = \langle p_z | \partial/\partial z | s \rangle$ and $Q = \langle p_z | \partial/\partial y | s \rangle = \langle p_z | \partial/\partial x | s \rangle$ neglecting all many centre integrals of these forms since their contribution is small [16]. We also neglect ligand-ligand overlap in Eq. (2) [3]. The integrals of type Q are zero by symmetry arguments [16] while those of type P are not and are therefore retained in the expressions (Eq. 4).

Following Tinkham [2] we express R 's defined in Eq. (1), as products of normalization constants

$$\begin{aligned}
 R_1 &= N_{a_1} N_{e_\xi}; & R_2 &= N_{b_1} N_{e_\xi}; & R_3 &= N_{b_2} N_{e_\xi}; & R_4 &= N_{b_1} N_{b_2}; \\
 R_5 &= N_{e_\xi} N_{e_\eta} \quad (5)
 \end{aligned}$$

where R_1, R_2, \dots, R_5 are defined analogously to the k 's in Eq. (4).

However, if one uses Missetich and Buch's approximation [7], the expressions of R 's are of the type

$$R_1 = N_{a_1} N_{e_\xi} \left[1 - \left\{ \frac{\lambda \mu_3 D}{\sqrt{3}} - \frac{\gamma \mu_3 A}{\sqrt{6}} - \frac{1}{\sqrt{2}} (\lambda \gamma_3 - \gamma \lambda_3) \right\} \frac{\zeta_b}{\zeta_d} \right] \quad (6)$$

corresponding to R_1 in Eq. (5) and where ζ_b is the spin-orbit coupling constant of the ligand atom and ζ_d that of the central metal ion. This type of expression is useful in compounds involving Br^- as the ligand (where ζ_b for $\text{Br}^- = 2200 \text{ cm}^{-1}$ [7]). In general $\zeta_b \ll \zeta_d$ and therefore the expression given in Eq. (6) reduces to Eq. (5).

4. Estimation of Mixing Coefficients

Mixing coefficients occurring in the antibonding MO's (Eq. (2)) are estimated from the expressions of k 's and R 's (Eqs. (4) and (5)) for the complexes Caesium tetrachlorocuprate(II) Cs_2CuCl_4 ; tetramethylammonium tetrachlorocuprate(II) $[(\text{CH}_3)_4\text{N}]_2\text{CuCl}_4$ and trimethylbenzyl ammonium tetrachlorocuprate(II) $[(\text{CH}_3)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{N}]_2\text{CuCl}_4$ using experimental information from X-ray structure [8, 9] (in calculating p , cf. Fig. 1), single crystal magnetic anisotropy [11], epr [10] and spectral results [12] of these compounds.

The procedure followed is: first reduction factors k 's and R 's of these compounds are found by fitting the experimental values of magnetic anisotropy and anisotropic g 's and energy level separations from spectral work to the theoretical expressions for the ionic anisotropic g 's and K 's (principal magnetic susceptibilities) in D_{2d} symmetry given in [18, 19]. The values of the reduction factors k_{\parallel} , k_{\perp} , R_{\parallel} and R_{\perp} so estimated are heretofore to be referred as experimentally estimated values and their correspondence with the expressions in Eqs. (4) and (5) are given in Table 1.

Now, the estimation of the mixing coefficients γ , λ , ... etc. using the experimentally estimated values of k 's and R 's (Table 1) and the relevant equations (Eqs. (4) and (5)) require the simultaneous solution of a set of non-linear algebraic equations. Therefore, we reduce the number of unknowns (mixing coefficients λ_1 , γ_2 , λ_2 , γ_3 , λ_3 , μ_3 ; overlap integrals S_1 , S_2 , S_3 ; the integral P and the value of the coordinate p) to the number of known quantities (values of k 's and R 's) in the following way:

(i) The value of " p " is calculated [16] using X-ray structural data for CuCl_4^{2-} ion in the above mentioned complexes [8, 9]. The values of the diatomic integrals S_1 , S_2 and S_3 are calculated using appropriate expressions [15] and the program PSJ3 [16]. The value of the integral P is obtained from the appropriate expression for a particular type of radial function for the metal ion (Cu^{+2}) and the ligand (Cl^-) orbitals using the program PINTGL [16].

(ii) The number of mixing coefficients is reduced to four by putting

$$\lambda_2 \approx \frac{\gamma_2}{3}$$

since π -overlap is usually one third of the σ -type overlap for the same pair of atomic orbitals [17], and also,

$$\mu_3 \approx \lambda_3$$

so that we have four unknown quantities in all i.e. λ_1 , γ_2 , γ_3 and λ_3 .

The resulting equations are then solved by a method of successive approximations, using the program D2DCOF [16], yielding values of the mixing coefficients (λ_1 , γ_2 , γ_3 , λ_3) and k_{\parallel} , k_{\perp} , R_{\parallel} , R_{\perp} nearest to the experimentally estimated values of k 's and R 's (cf. Table 1). The results are given in Table 1.

Table 1. Mixing coefficients for CuCl_4^{2-}

1. Cs_2CuCl_4 Using Original Exptal Values of k_{\parallel}^a k_{\perp}^a R_{\parallel}^a R_{\perp}^a (Values in Brackets are Exptal)								
Basis Orbitals	λ_1	γ_2	γ_3	λ_3	R_{\parallel} (0.73)	R_{\perp} (0.70)	k_{\parallel} (0.81)	k_{\perp} (0.72)
S.T.O.	0.646	0.05	0.05	0.71	0.812	0.716	0.739	0.701
Clementi and Raimondi	0.8	0.01	0.01	0.7	0.7697	0.711	0.749	0.711
Burns	0.69	0.01	0.01	0.703	0.797	0.709	0.754	0.710
Richardson	0.67	0.01	0.01	0.70	0.798	0.710	0.746	0.712
2. Cs_2CuCl_4 Using Refitted Values of k_{\parallel} k_{\perp} R_{\parallel} R_{\perp}								
Basis Orbitals	λ_1	λ_2	γ_3	λ_3	R_{\parallel} (0.81)	R_{\perp} (0.76)	k_{\parallel} (0.73)	k_{\perp} (0.70)
S.T.O.	0.66	0.06	0.35	0.63	0.809	0.761	0.731	0.695
Clementi and Raimondi	0.46	0.54	0.67	0.17	0.811	0.758	0.730	0.702
Burns	0.69	0.15	0.58	0.53	0.805	0.759	0.732	0.699
Richardson	0.67	0.12	0.45	0.59	0.809	0.759	0.728	0.701

^a $k_{\parallel} \equiv k_4$, $k_{\perp} \equiv k_3$, $R_{\parallel} \equiv R_4$, $R_{\perp} \equiv R_3$.

Structural Parameters for Cs_2CuCl_4

$\alpha = 62.05^{\circ}$ [8]; $R = 0.2215$ nm (cf. Fig. 1) [8]. $p = 0.75036925$

$A = 0.33142185$; $B = 0.88335681$; $D = 0.62462753$; $E = 0.46870124$; $M = 0.11320457$

Overlap Integrals and P Integral

Basis Functions	S_1	S_2	S_3	P
Slater type [20]	0.13952506	0.14825398	0.061057858	-0.36886328
Multiple basis Cu^{++} (23)				
Cl^- [24]	0.074147642	0.10832310	0.053064119	-0.41735250

Numerical values of structural parameters and other integrals for the remaining compounds are available on request.

5. Comment on the Relative Values of k and R

Preliminary attempt to determine the mixing coefficients led to the following difficulty – wherever the experimentally estimated values of k 's were greater than R 's [18, 19] it was found that the numerical method for estimating mixing coefficient did not yield an agreement of calculated k 's and R 's with the experimentally estimated k 's and R 's.

It is apparent from the expressions of k 's and R 's (Eqs. (4) and (5)) that k is R times a factor of the form

$$[1 - \sum_i \lambda_i G_i + \alpha \lambda_i \lambda_j] \quad (7)$$

where λ_i , λ_j are mixing coefficients, G_i a group overlap integral [15] and α a term involving numerical quantities and the integral P (cf. Eq. (4)) and where

the integral P is negative. Now, since the value of the factor (7) is less than unity, one must have, in the present approximation, $k < R$, a result which has not been pointed out as yet [3]. If the expression for R is considered to be that given in Eq. (6) one can still have $k < R$, since in the expression for R the normalisation constants are multiplied by a factor such as

$$\left[1 - \left\{ \frac{\lambda\mu_3 D}{\sqrt{3}} - \frac{\gamma\mu_3 A}{\sqrt{6}} - \frac{1}{\sqrt{2}}(\lambda\gamma_3 - \gamma\lambda_3) \right\} \frac{\zeta_p}{\zeta_d} \right] \quad (8)$$

where the numerical value is larger than that of (7) especially since ζ_p for ligands like O, N, Cl^- is very much less than ζ_d of the metal ion.

It may also be pointed out that the same relation $k < R$ holds [16] when one uses the expressions of $k_{\sigma\pi}$, $k_{\pi\pi}$, $R_{\sigma\pi}$ and $R_{\pi\pi}$ given in [3] for O_h symmetry. The result $k < R$ thus minimises the uncertainty in the choice of parameters like k 's and R 's while fitting experimentally obtained data with the theoretical expressions for anisotropic g 's and magnetic susceptibilities (k 's). In view of this result, we have refitted the experimental values of ionic anisotropies and resonance ionic g -values in the complexes, where necessary, satisfying the condition $k < R$ (Table 1).

6. Effect of Radial Function on Mixing Coefficients

The choice of different radial functions (both single [20, 21, 22] and multiple basis radial functions of Cu^{++} [23] and Cl^- [24] being used (cf. Table 1)) affects the values of the overlap integrals, the P integral and also the mixing coefficients but the changes occurring in the values of the mixing coefficients were not found to be significant.

During this work, it was felt that a certain amount of confusion exists regarding the values of integrals of the types P and Q [3] defined in Sect. 3. P integrals for certain specific cases [6, 25, 26] are known but no general formulae for these integrals exists. Considering first the one centre case one notes that integrals of form Q are zero on symmetry grounds [16] while those of form P have values dependent on the choice of radial functions for p and s -orbitals. With hydrogen like radial functions, one can show that the P integral must be identically zero while for Slater type radial functions this is not the case. We document the following expression for P in the one centre case

$$P = \frac{1}{\sqrt{3}} \frac{(2\zeta_a)^{n_a+1/2} (2\zeta_b)^{n_b+1/2}}{(2n_a!)^{1/2} (2n_b!)^{1/2}} \frac{(n_a + n_b)!}{(\zeta_a + \zeta_b)^{n_a+n_b+1}} \left\{ \frac{\zeta_a(n_b-1) + \zeta_b(n_b+1)}{n_a + n_b} \right\}$$

where n_a , n_b are the principal quantum numbers and ζ_a , ζ_b the orbital exponents, respectively, of the p_z and s orbital. Using Slater type radial functions for p_z and s orbital with $\partial/\partial z$ referred to the same centre as the s orbital we obtain the following expression for the two-centre P integral

$$P = \frac{\zeta_b}{\sqrt{3}} \left[\frac{2(n_b-1)}{\sqrt{2n_b(2n_b-1)}} S(n_a p_\sigma, n_b-1 p_\sigma) - S(n_a p_\sigma, n_b p_\sigma) \right]$$

where $S(n_a p_\sigma, n_b - 1 p_\sigma)$ and $S(n_a p_\sigma, n_b p_\sigma)$ are diatomic overlap integrals [15]. A similar expression results if we use hydrogenlike radial function for the orbitals.

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