Expression of monocentric repulsion integrals in the basis of *s,p,d* atomic orbitals

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Monocentric electron repulsion integrals arising in the *s,p,d* basis of atomic orbitals were expressed in terms of the Slater—Condon parameters F^k_{ab} and G^k_{ab} and in terms of the radial integrals R^k_{abcd}. The total number of such integrals in the *s,p,d* basis is 6561, from which 753 are non-zero.

Methods in quantum chemistry, which explicitly include electron repulsion, contain expressions in which one finds electron repulsion integrals of the type

$$(ac|bd) = \int_{\tau_1}\int_{\tau_2} \chi_a^*(1)\,\chi_b^*(2)\,\frac{1}{r_{12}}\,\chi_c(1)\,\chi_d(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2. \qquad (1)$$

Different methods which use different degrees of approximations, neglect several types of these integrals. The use of the INDO method continues to increase. This method covers all the monocentric integrals of the type $(ac|bd)$, where a, b, c, and d are atomic orbitals (AO's) centred on the same atom. Expression of these integrals by the Slater—Condon parameters is simple. As long as we use *s,p* AO's basis we do not come across any problem. There are many attempts to extend the INDO method to the basis of *s,p,d*, AO's and to interpret the compounds of transition metals, where *s,p,d* basis is unavoidable [1—3]. However, none of the mentioned papers uses a complete set of non-zero monocentric repulsion integrals in the *s,p,d* basis, although their expression by means of the Slater—Condon parameters is simple. The number of all monocentric repulsion integrals, including the zero ones, in this basis is $9^4 = 6561$; when using the basis of *s,p* AO's this number is only $4^4 = 256$.

Calculation of monocentric repulsion integrals

The method of calculation of monocentric repulsion integrals of the type $(ac|bd)$ is well known and has been described *e.g.* in [4, 5]. Integrals of the type (*1*) can be divided in the radial and the angular part if we consider that $1/r_{12}$ can be expanded into a series of spherical functions and the complex atomic orbitals may be written as a product of their radial and angular parts. Then we get [4, 5]

$$(ac|bd) = \sum_{k=0}^{\infty} C^k(l_a m_a, l_c m_c)\; C^k(l_d m_d, l_b m_b)\; R^k(a,b,c,d), \qquad (2)$$

where

$$R^k(a,b,c,d) = R^k_{abcd} = \int_0^\infty\int_0^\infty R^*_{n_a l_a}(r_1) R^*_{n_b l_b}(r_2)\; R_{n_c l_c}(r_1)\cdot R_{n_d l_d}(r_2)\frac{2r_<^k}{r_>^{k+1}}\, r_1^2\, r_2^2\,\mathrm{d}r_1\,\mathrm{d}r_2, \qquad (3)$$

Table 1

Expression of real atomic orbitals in terms of linear combination of complex atomic orbitals

$$
\begin{aligned}
|s\rangle &= |0,0\rangle \\
|x\rangle &= 1/\sqrt{2}(|1,-1\rangle - |1,1\rangle) \\
|y\rangle &= i/\sqrt{2}(|1,-1\rangle + |1,1\rangle) \\
|z\rangle &= |1,0\rangle \\
|z^2\rangle &= |2,0\rangle \\
|x^2 - y^2\rangle &= 1/\sqrt{2}(|2,2\rangle + |2,-2\rangle) \\
|xy\rangle &= i/\sqrt{2}(|2,-2\rangle - |2,2\rangle) \\
|xz\rangle &= 1/\sqrt{2}(|2,-1\rangle - |2,1\rangle) \\
|yz\rangle &= i/\sqrt{2}(|2,-1\rangle + |2,1\rangle)
\end{aligned}
$$

Table 2

Non-zero monocentric electron repulsion integrals which originate in s,p,d basis

1. F^0_{ss} (1)
   $(s,s|s,s)$
2. F^0_{sp} (6)
   $(s,s|z,z)$, $(s,s|x,x)$, $(s,s|y,y)$
3. $1/3\ G^1_{sp}$ (12)
   $(s,z|s,z)$, $(s,x|s,x)$, $(s,y|s,y)$
4. $F^0_{pp} + 4/25\ F^2_{pp}$ (3)
   $(z,z|z,z)$, $(x,x|x,x)$, $(y,y|y,y)$
5. $F^0_{pp} - 2/25\ F^2_{pp}$ (6)
   $(z,z|x,x)$, $(z,z|y,y)$, $(x,x|y,y)$
6. $3/25\ F^2_{pp}$ (12)
   $(z,x|z,x)$, $(z,y|z,y)$, $(x,y|x,y)$
7. $1/15\ G^1_{pd} + 18/245\ G^3_{pd}$ (8)
   $(x,z^2|x,z^2)$, $(y,z^2|y,z^2)$
8. $-\sqrt{3}/15\ G^1_{pd} - \sqrt{27}/245\ G^3_{pd}$ (24)
   $(x,z^2|x,x^2 - y^2)$, $(x,z^2|y,xy)$, $(x,xy|z^2,y)$
9. $1/5\ G^1_{pd} - 21/245\ G^3_{pd}$ (8)
   $(x,x^2 - y^2|y,xy)$
10. $-1/5\ G^1_{pd} + 21/245\ G^3_{pd}$ (8)
    $(x,xy|y,x^2 - y^2)$
11. $F^0_{pd} - 2/35\ F^2_{pd}$ (4)
    $(x,x|z^2,z^2)$, $(y,y|z^2,z^2)$
12. $-\sqrt{12}/35\ F^2_{pd}$ (12)
    $(x,x|z^2,x^2 - y^2)$, $(x,y|z^2,xy)$
13. $\sqrt{3}/15\ G^1_{pd} + \sqrt{27}/245\ G^3_{pd}$ (8)
    $(y,z^2|y,x^2 - y^2)$
14. $4/15\ G^1_{pd} + 27/245\ G^3_{pd}$ (4)
    $(z,z^2|z,z^2)$
15. $3/49\ G^3_{pd}$ (48)
    $(z,x^2 - y^2|z,x^2 - y^2)$, $(z,xy|z,xy)$, $(x,yz|x,yz)$, $(y,xz|y,xz)$, $(z,x^2 - y^2|x,xz)$, $(z,xy|x,yz)$, $(z,xy|y,xz)$, $(x,yz|y,xz)$

16. $1/5\ G^1_{pd} + 24/245\ G^3_{pd}$ (32)
$(z,xz|z,xz)$, $(z,yz|z,yz)$, $(x,xy|x,xy)$, $(x,x^2-y^2|x,x^2-y^2)$, $(x,xz|x,xz)$, $(y,xy|y,xy)$, $(y,yz|y,yz)$, $(y,x^2-y^2|y,x^2-y^2)$

17. $12/15\ G^1_{pd} - \sqrt{243}/245\ G^3_{pd}$ (16)
$(z,z^2|x,xz)$, $(z,z^2|y,yz)$

18. $1/5\ G^1_{pd} - 6/245\ G^3_{pd}$ (32)
$(z,xz|x,x^2-y^2)$, $(z,yz|x,xy)$, $(z,xz|y,xy)$, $(x,xz|y,yz)$

19. $-3/49\ G^3_{pd}$ (8)
$(z,x^2-y^2|y,yz)$

20. $-\sqrt{3}/15\ G^1_{pd} + \sqrt{432}/245\ G^3_{pd}$ (16)
$(z,yz|y,z^2)$, $(z,xz|x,z^2)$

21. $-1/5\ G^1_{pd} + 6/245\ G^3_{pd}$ (8)
$(z,yz|y,x^2-y^2)$

22. $F^0_{pd} + 4/35\ F^2_{pd}$ (2)
$(z,z|z^2,z^2)$

23. $\sqrt{3}/35\ F^2_{pd}$ (16)
$(z,x|z^2,xz)$, $(z,y|z^2,yz)$

24. $F^0_{pd} - 4/35\ F^2_{pd}$ (8)
$(z,z|x^2-y^2,x^2-y^2)$, $(z,z|xy,xy)$, $(x,x|yz,yz)$, $(y,y|xz,xz)$

25. $3/35\ F^2_{pd}$ (32)
$(z,x|x^2-y^2,xz)$, $(z,x|xy,yz)$, $(z,y|xy,xz)$, $(x,y|xz,yz)$

26. $-3/35\ F^2_{pd}$ (8)
$(z,y|x^2-y^2,yz)$

27. $F^0_{pd} + 2/35\ F^2_{pd}$ (16)
$(z,z|xz,xz)$, $(z,z|yz,yz)$, $(x,x|xy,xy)$, $(x,x|x^2-y^2,x^2-y^2)$, $(x,x|xz,xz)$, $(y,y|xy,xy)$, $(y,y|yz,yz)$, $(y,y|x^2-y^2,x^2-y^2)$

28. $\sqrt{12}/35\ F^2_{pd}$ (4)
$(y,y|z^2,x^2-y^2)$

29. $1/5\ G^2_{sd}$ (20)
$(s,z^2|s,z^2)$, $(s,x^2-y^2|s,x^2-y^2)$, $(s,xy|s,xy)$, $(s,xz|s,xz)$, $(s,yz|s,yz)$

30. F^0_{sd} (10)
$(s,s|z^2,z^2)$, $(s,s|x^2-y^2,x^2-y^2)$, $(s,s|xy,xy)$, $(s,s|xz,xz)$, $(s,s|yz,yz)$

31. $F^0_{dd} + 4/49\ F^2_{dd} + 36/441\ F^4_{dd}$ (5)
$(z^2,z^2|z^2,z^2)$, $(x^2-y^2,x^2-y^2|x^2-y^2,x^2-y^2)$, $(xy,xy|xy,xy)$, $(xz,xz|xz,xz)$, $(yz,yz|yz,yz)$

32. $4/49\ F^2_{dd} + 15/441\ F^4_{dd}$ (8)
$(z^2,x^2-y^2|z^2,x^2-y^2)$, $(z^2,xy|z^2,xy)$

33. $1/49\ F^2_{dd} + 30/441\ F^4_{dd}$ (8)
$(z^2,xz|z^2,xz)$, $(z^2,yz|z^2,yz)$

34. $F^0_{dd} - 4/49\ F^2_{dd} + 6/441\ F^4_{dd}$ (4)
$(z^2,z^2|x^2-y^2,x^2-y^2)$, $(z^2,z^2|xy,xy)$

35. $\sqrt{3}/49\ F^2_{dd} - \sqrt{75}/441\ F^4_{dd}$ (24)
$(z^2,xz|x^2-y^2,xz)$, $(z^2,xz|xy,yz)$, $(z^2,yz|xy,xz)$

36. $-\sqrt{3}/49\ F^2_{dd} + \sqrt{75}/441\ F^4_{dd}$ (8)
$(z^2,yz|x^2-y^2,yz)$

37. $F^0_{dd} + 2/49\ F^2_{dd} - 24/441\ F^4_{dd}$ (4)
$(z^2,z^2|xz,xz)$, $(z^2,z^2|yz,yz)$

38. $-\sqrt{12}/49\ F^2_{dd} + \sqrt{300}/441\ F^4_{dd}$ (12)
$(z^2,x^2-y^2|xz,xz)$, $(z^2,xy|xz,yz)$

39. $\sqrt{12}/49\ F^2_{dd} - \sqrt{300}/441\ F^4_{dd}$ (4)
$(z^2,x^2 - y^2|yz,yz)$

40. $35/441\ F^4_{dd}$ (4)
$(x^2 - y^2,xy|x^2 - y^2,xy)$

41. $3/49\ F^2_{dd} + 20/441\ F^4_{dd}$ (20)
$(xy,xz|xy,xz)$, $(xy,yz|xy,yz)$, $(xz,yz|xz,yz)$, $(x^2 - y^2,xz|x^2 - y^2,xz)$, $(x^2 - y^2,yz|x^2 - y^2,yz)$

42. $F^0_{dd} + 4/49\ F^2_{dd} - 34/441\ F^4_{dd}$ (2)
$(x^2 - y^2,x^2 - y^2|xy,xy)$

43. $3/49\ F^2_{dd} - 15/441\ F^4_{dd}$ (8)
$(x^2 - y^2,xz|xy,yz)$

44. $-3/49\ F^2_{dd} + 15/441\ F^4_{dd}$ (8)
$(x^2 - y^2,yz|xy,xz)$

45. $F^0_{dd} - 2/49\ F^2_{dd} - 4/441\ F^4_{dd}$ (10)
$(xy,xy|xz,xz)$, $(xy,xy|yz,yz)$, $(xz,xz|yz,yz)$, $(x^2 - y^2,x^2 - y^2|xz,xz)$, $(x^2 - y^2,x^2 - y^2|yz,yz)$

46. $2/\sqrt{245}\ R^2_{sddd}$ (4)
$(s,z^2|z^2,z^2)$

47. $-2/\sqrt{245}\ R^2_{sddd}$ (24)
$(s,x^2 - y^2|z^2,x^2 - y^2)$, $(s,xy|z^2,xy)$, $(s,z^2|x^2 - y^2,x^2 - y^2)$, $(s,z^2|xy,xy)$

48. $1/\sqrt{245}\ R^2_{sddd}$ (24)
$(s,xz|z^2,xz)$, $(s,yz|z^2,yz)$, $(s,z^2|xz,xz)$, $(s,z^2|yz,yz)$

49. $\sqrt{3}/\sqrt{245}\ R^2_{sddd}$ (36)
$(s,xz|x^2 - y^2,xz)$, $(s,xz|xy,yz)$, $(s,yz|xy,xz)$, $(s,xy|xz,yz)$, $(s,x^2 - y^2|xz,xz)$

50. $-\sqrt{3}/\sqrt{245}\ R^2_{sddd}$ (12)
$(s,yz|x^2 - y^2,yz)$, $(s,x^2 - y^2|yz,yz)$

51. $-1/\sqrt{125}\ R^2_{sppd}$ (8)
$(s,z^2|x,x)$, $(s,z^2|y,y)$

52. $-\sqrt{3}/\sqrt{45}\ R^1_{sppd}$ (8)
$(s,y|y,x^2 - y^2)$

53. $-\sqrt{3}/\sqrt{125}\ R^2_{sppd}$ (4)
$(y,y|s,x^2 - y^2)$

54. $2/\sqrt{45}\ R^1_{spdd}$ (8)
$(z,s|z,z^2)$

55. $\sqrt{3}/\sqrt{45}\ R^1_{sppd}$ (56)
$(z,s|x,xz)$, $(z,xz|x,s)$, $(z,s|y,yz)$, $(z,yz|y,s)$, $(x,s|x,x^2 - y^2)$, $(x,s|y,xy)$, $(x,xy|s,y)$

56. $2/\sqrt{125}\ R^2_{sppd}$ (4)
$(z,z|s,z^2)$

57. $\sqrt{3}/\sqrt{125}\ R^2_{sppd}$ (28)
$(z,x|s,xz)$, $(z,y|s,yz)$, $(x,x|s,x^2 - y^2)$, $(x,y|s,xy)$

58. $-1/\sqrt{45}\ R^1_{sppd}$ (16)
$(x,s|x,z^2)$, $(y,s|y,z^2)$

The numerals in brackets represent the number of all possible integrals of the given value. Only one integral from each type is shown, because: $(ab|cd) = (ab|dc) = (ba|cd) = (ba|dc) = (cd|ab) = (cd|ba) = (dc|ab) = (dc|ba)$.

$$C^k(l_a m_a, l_c m_c) = \sum_{m=-k}^{+k} \sqrt{\frac{(k-|m|)!}{(k+|m|)!}} \int_0^{\pi} \int_0^{2\pi} Y^*_{l_a m_a}(\vartheta_1,\varphi_1) \cdot$$

$$\cdot\, Y_{l_c m_c}(\vartheta_1,\varphi_1)\, P_k^{|m|}(\cos\vartheta_1) \exp(im\varphi_1) \sin\vartheta_1 \,\mathrm{d}\vartheta_1 \,\mathrm{d}\varphi_1 \qquad (4)$$

and a similar expression for $C^k(l_d m_d, l_b m_b)$. The values of the integrals of angular parts $C^k(l_a m_a, l_c m_c)$ and $C^k(l_d m_d, l_b m_b)$ for s,p,d orbitals have been tabulated [4, 5].

Integrals of the radial part of the types $R^k(a,b,a,b)$ and $R^k(a,b,b,a)$ are the Slater—Condon parameters and usually are represented by

$$R^k(a,b,a,b) = R^k_{abab} = F^k_{ab}, \qquad (5)$$

$$R^k(a,b,b,a) = R^k_{abba} = G^k_{ab}. \qquad (6)$$

These integrals occur in expressions for the differences of energy levels of atoms and they can be determined by an analysis of the atomic spectra [6, 7]. In MO calculations it is advantageous to use the real atomic orbitals as a basis. These are the linear combinations of the complex atomic orbitals (Table 1). Then it is necessary to substitute the appropriate linear combinations into expression (*1*). After rearranging we obtain repulsion integrals in a basis of complex atomic orbitals, for which the coefficients $C^k(l_i m_i, l_j m_j)$ are published [4, 5]. Since the linear combination in the formation of real AO's from complex AO's concerns only their angular parts and the radial parts remain unchanged, the shown procedure is sufficient for the calculation of angular coefficients $C^k(l_i m_i, l_j m_j)$, while the radial integrals will be the same in both bases.

This procedure was applied in the calculation of all monocentric repulsion integrals, which arise in the s,p,d AO's basis. From 6561 possible integrals 753 are non-zero (Table 2). Non-zero integrals can be categorized into 58 groups which contain integrals of equal value. Not all of the non-zero integrals can be expressed in terms of the Slater—Condon parameters because several types of integrals have the radial part which does not belong among the Slater—Condon parameters.

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