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Ligand Field Matrix Elements for *f*-Electrons

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The calculations of the ligand field splitting of *f*-electrons in an electrostatic model where ligands are represented as point charges follow a similar procedure developed for the calculations of the ligand field splitting of *d*-electrons in transition-metal complexes. In the latter case the formulae for the ligand field matrix elements $H_{ik} = \langle m_i \mid V \mid m_k \rangle$, where V is the electrostatic potential

$$V = \sum_j \frac{e^2}{r_{ej}}$$

$$(r_{ej} = \text{distance electron-ligand } r_j, \vartheta_j, \varphi_j)$$

and m_i, m_k, designate different *d*-orbitals, have been given by HARTMANN and KÖNIG [*1*] for ligands situated in general positions*.

Here we wish to give a list of ligand field matrix elements H_{ik} between *f*-orbitals in the electrostatic perturbation due to point charges situated in a general position $(r_j, \vartheta_j, \varphi_j)$.

The ligand field matrix is *hermitian* i.e. $H_{ik} = H_{ki}^*$, and in addition it is symmetric or antisymmetric with respect to the other diagonal, due to:

$$\langle Y_l^m \mid V \mid Y_l^{m'} \rangle = (-1)^{m-m'} \langle Y_l^{-m'} \mid V \mid Y_l^{-m} \rangle .$$

As the basis for the evaluation of the matrix elements we used the form of orbitals with well defined quantum number m. Such a form is a useful basis for ligand fields with axial symmetry: C_n, C_{nv}, D_{nh} if $n = 5{,}7$ and higher. In these cases pairs of orbitals with the same absolute value of m remain degenerate. The quantum number m retains its meaning. In cases $n = 2, 3, 4, 6$ this degeneracy no longer holds. Then another set of functions: $x(5z^2 - r^2)$, $y(5z^2 - r^2)$ etc. makes a better basis, since these functions are symmetric and antisymmetric on reflections in coordinate *planes*, which now form symmetry elements. Similarly in cubic point groups yet another orbitals:

$$x(5x^2 - 3r^2), \quad y(5y^2 - 3r^2) \text{ and } z(5z^2 - 3r^2) \text{ etc.}$$

form most suitable basis for setting up the secular equations. The ligand field

* Similar formulae were also given later by COMPANION and KOMARINSKY [*2*], who used *d*-orbitals in their real form. Corrections to the matrix elements are given in Ref. [*3*].

Table. *Matrix elements of the electrostatic potential due to ligands situated in general positions. The integrals G_n are defined as follows:*

$$G_n = \int_0^\infty R^2(r) \frac{r_<^n}{r_>^{n+1}} r^2 dr$$

where $R(r)$ is the radial part of an f-electron wavefunction. The summation is over all ligands

$\langle 0 \mid V \mid 0 \rangle$	$=$	$e^2 \sum_j \{G_0 + 2/15\,(3\cos^2\vartheta_j - 1)\,G_2 + 1/44\,(35\cos^4\vartheta_j - 30\cos^2\vartheta_j + 3)\,G_4 + 25/1716\,(231\cos^6\vartheta_j - 315\cos^4\vartheta_j + 105\cos^2\vartheta_j - 5)G_6\}$
$\langle \pm 1 \mid V \mid \pm 1 \rangle$	$=$	$e^2 \sum_j \{G_0 + 1/10\,(3\cos^2\vartheta_j - 1)\,G_2 + 1/264\,(35\cos^4\vartheta_j - 30\cos^2\vartheta_j + 3)\,G_4 - 25/2288\,(231\cos^6\vartheta_j - 315\cos^4\vartheta_j + 105\cos^2\vartheta_j - 5)G_6\}$
$\langle \pm 2 \mid V \mid \pm 2 \rangle$	$=$	$e^2 \sum_j \{G_0 - 7/264\,(35\cos^4\vartheta_j - 30\cos^2\vartheta_j + 3)\,G_4 + 5/1144\,(231\cos^6\vartheta_j - 315\cos^4\vartheta_j + 105\cos^2\vartheta_j - 5)\,G_6\}$
$\langle \pm 3 \mid V \mid \pm 3 \rangle$	$=$	$e^2 \sum_j \{G_0 - 1/6\,(3\cos^2\vartheta_j - 1)\,G_2 + 1/88\,(35\cos^4\vartheta_j - 30\cos^2\vartheta_j + 3)\,G_4 - 5/6864\,(231\cos^6\vartheta_j - 315\cos^4\vartheta_j + 105\cos^2\vartheta_j - 5)\,G_6\}$
$\langle 3 \mid V \mid 2 \rangle$	$=$	$e^2 \sum_j \sqrt{6}/6 \exp(-i\varphi_j) \sin\vartheta_j \cos\vartheta_j \{-G_2 + 5/22\,(7\cos^2\vartheta_j - 3)\,G_4 - 35/1144\,(33\cos^4\vartheta_j - 30\cos^2\vartheta_j + 5)\,G_6\}$
$\langle 3 \mid V \mid 1 \rangle$	$=$	$e^2 \sum_j \sqrt{15}/2 \exp(-i2\varphi_j) \sin^2\vartheta_j \{-1/15\,G_2 + 1/22\,(7\cos^2\vartheta_j - 1)\,G_4 - 35/3432\,(33\cos^4\vartheta_j - 18\cos^2\vartheta_j + 1)\,G_6\}$
$\langle 3 \mid V \mid 0 \rangle$	$=$	$e^2 \sum_j \sqrt{5}\cdot 7/44 \exp(-i3\varphi_j) \sin^3\vartheta_j \cos\vartheta_j \{G_4 - 5/26\,(11\cos^2\vartheta_j - 3)\,G_6\}$
$\langle 3 \mid V \mid -1 \rangle$	$=$	$e^2 \sum_j \sqrt{15}\cdot 7/88 \exp(-i4\varphi_j) \sin^4\vartheta_j \{1/3\,G_4 - 5/26\,(11\cos^2\vartheta_j - 1)\,G_6\}$
$\langle 3 \mid V \mid -2 \rangle$	$= -$	$e^2 \sum_j \sqrt{6}\cdot 385/2288 \exp(-i5\varphi_j) \sin^5\vartheta_j \cos\vartheta_j\, G_6$
$\langle 3 \mid V \mid -3 \rangle$	$= -$	$e^2 \sum_j 385/2288 \exp(-i6\varphi_j) \sin^6\vartheta_j\, G_6$
$\langle 2 \mid V \mid -2 \rangle$	$=$	$e^2 \sum_j 35/88 \exp(-i4\varphi_j) \sin^4\vartheta_j \{1/3\,G_4 + 3/13\,(11\cos^2\vartheta_j - 1)\,G_6\}$
$\langle 1 \mid V \mid -1 \rangle$	$= -$	$e^2 \sum_j \exp(-i2\varphi_j) \sin^2\vartheta_j \{1/5\,G_2 + 5/66\,(7\cos^2\vartheta_j - 1)\,G_4 + 175/2288\,(33\cos^4\vartheta_j - 18\cos^2\vartheta_j + 1)\,G_6\}$
$\langle 1 \mid V \mid 0 \rangle$	$= -$	$e^2 \sum_j \sqrt{3} \exp(-i\varphi_j) \sin\vartheta_j \cos\vartheta_j \{1/15\,G_2 + 5/132\,(7\cos^2\vartheta_j - 3)\,G_4 + 175/3432\,(33\cos^4\vartheta_j - 30\cos^2\vartheta_j + 5)\,G_6\}$
$\langle 2 \mid V \mid 1 \rangle$	$=$	$e^2 \sum_j \sqrt{10} \exp(-i\varphi_j) \sin\vartheta_j \cos\vartheta_j \{-1/10\,G_2 - 1/33\,(7\cos^2\vartheta_j - 3)\,G_4 + 35/2288\,(33\cos^4\vartheta_j - 30\cos^2\vartheta_j + 5)\,G_6\}$
$\langle 2 \mid V \mid 0 \rangle$	$=$	$e^2 \sum_j \sqrt{30}/6 \exp(-i2\varphi_j) \sin^2\vartheta_j \{-1/5\,G_2 - 1/44\,(7\cos^2\vartheta_j - 1)\,G_4 + 35/572\,(33\cos^4\vartheta_j - 18\cos^2\vartheta_j + 1)\,G_6\}$
$\langle 2 \mid V \mid -1 \rangle$	$=$	$e^2 \sum_j \sqrt{10}\cdot 7/44 \exp(-i3\varphi_j) \sin^3\vartheta_j \cos\vartheta_j \{1/3\,G_4 + 15/52\,(11\cos^2\vartheta_j - 3)\,G_6\}$

matrix elements in these latter cases may be obtained from those listed in table using a transformation procedure: $\boldsymbol{H}' = \boldsymbol{T}^{-1} \boldsymbol{H}\boldsymbol{T}$, where $\boldsymbol{T}$ transforms the old bases into a new one.

References

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