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# The angular dependence of the multipole–multipole interaction for energy transfer

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**Abstract.** The interaction between multipoles is not isotropic even in cubic systems. This results in the introduction of geometric reduction factors in the calculation of energy-transfer rates in crystals. We derive these reduction factors for the cases of dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole couplings and present a general procedure for their derivation in other cases. For the dipole–dipole case the geometric factor is independent of the distribution of the acceptor species, but for higher-order couplings, a significant angular dependence is found.

**Key words:** Energy transfer – Shell model – Multipolar interaction – Angular dependence – Elpasolite crystal

## 1 Introduction

In a recent series of papers we derived a discrete shell model for energy transfer and applied this model to the luminescence decay curves of excited electronic states of rare-earth ions in the cubic hexachloroelpasolite crystal $Cs_2NaLnCl_6$[1–3]. In the systems considered in these papers the dominant mechanism of energy transfer is dipole–dipole coupling. Direct calculation using a Cartesian basis shows that, in this case, the energy-transfer rate is independent of the precise angular distribution of the acceptors around the donor although, of course, it does depend on the number and distance of these acceptors. In some cases we found experimentally that the interaction between donors and acceptors was apparently of shorter range than the $R^{-6}$dependence of a dipole–dipole interaction and this led us to consider the possibility of both higher-order couplings and the effect of a nonisotropic dielectric shielding factor. To consider these possibilities quantitatively it is necessary to calculate the effect of the angular dependence of the coupling of higher multipoles on the energy-transfer rates. This paper describes a method for calculating these quantities.

## 2 The shell model for energy transfer

In the presence of a single chemical type of optically active acceptor for the donor excitation energy, the energy-transfer processes are due to cross relaxation and within the shell model the luminescence decay curves following a $\delta$-function excitation pulse take the form [1]

$$I(t) = I(0)\exp(-k_0 t)\prod_{n=1}^{\text{shells}}\sum_{r_n=0}^{N_n} O_{r_n}^{N_n}(x) \times \exp\left[-G_n^{s_p}\left(\frac{R_1}{R_n}\right)^{s_p} r_n k^{\mathrm{CR}} t\right]. \quad (1)$$

$x$ is the mole fraction of the optically active ion, $R_n$ is the distance between the donor ion and an acceptor ion in the $n$th shell determined by the crystal structure, $k_0$ is the intrinsic decay rate involving radiative and nonradiative single-ion processes, and $k^{\mathrm{CR}}$ is the cross-relaxation rate from a donor ion to a single acceptor in the first shell. $s_p =$ 6, 8, or 10 for electric dipole vibronic–electric dipole vibronic (EDV–EDV) or magnetic dipole–magnetic dipole (MD–MD), electric dipole vibronic–electric quadrupole (EDV–EQ), and electric quadrupole–electric quadrupole (EQ–EQ) interactions, respectively. The index $p$ distinguishes between different coupling components for a given value of $s$. In octahedral symmetry the electric and magnetic dipole operators transform as the irreducible representation (irrep) $T_1$ and therefore only a single component exists for dipole–dipole coupling. The EQ operator transforms as the direct sum $E \oplus T_2$ and three (six) different components occur for EDV–EQ (EQ–EQ) coupling.

In our shell model we assume Förster–Dexter multipole–multipole interaction among donor and acceptor ions with the resonant cross-relaxation rate given by [4, 5]

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$$k_n^{\mathrm{CR}} = \frac{2\pi}{\hbar}\left|\langle DA'|\hat{H}_n|D'A\rangle\right|^2 \int f_{D'D}(E) f_{AA'}(E)\,\mathrm{d}E \ , \tag{2}$$

where the overlap integral contains normalized lineshape functions of donor emission and acceptor absorption transitions.

The donor–acceptor interaction Hamiltonian for each shell may be expanded in terms of spherical harmonics according to Carlson and Rushbrooke [6] as

$$\begin{aligned}\hat{\mathrm{H}}_n &= \frac{1}{4\pi\varepsilon_0\varepsilon_n} \\ &\times \sum_{k_1,k_2=0}^{\infty} \sum_{q_1=-k_1}^{k_1} \sum_{q_2=-k_2}^{k_2} \frac{1}{R_n^{k_1+k_2+1}} T_{-(q_1+q_2)}^{(k_1+k_2)} D_{q_1}^{(k_1)} \\ &\times (r_{\mathrm{D}}, \vartheta_{\mathrm{D}}, \varphi_{\mathrm{D}}) D_{q_2}^{(k_2)}(r_{\mathrm{A}}, \vartheta_{\mathrm{A}}, \varphi_{\mathrm{A}}) \ ,\end{aligned} \tag{3}$$

where $\varepsilon_n$ is the nonisotropic dielectric shielding factor. $D_{q_1}^{(k_1)}(r_{\mathrm{D}}, \vartheta_{\mathrm{D}}, \varphi_{\mathrm{D}})$ and $D_{q_2}^{(k_2)}(r_{\mathrm{A}}, \vartheta_{\mathrm{A}}, \varphi_{\mathrm{A}})$ are the corresponding Garstang tensor operators associated with the transition multipoles of donor and acceptor transitions and are given by [7]

$$D_q^{(k)}(r, \vartheta, \varphi) = -er^k C_q^{(k)}(\vartheta, \varphi) \ , \tag{4}$$

where $e$ is the electron charge and the $C_q^{(k)}(\vartheta, \varphi)$ are the standard Racah tensor operators [8]. The geometric tensor

$$T_{-(q_1+q_2)}^{(k_1+k_2)} = t_{-(q_1+q_2)}^{(k_1+k_2)} C_{-(q_1+q_2)}^{(k_1+k_2)}(\Theta_n, \Phi_n) \tag{5}$$

contains the angular dependence of the interaction between the donor and an acceptor at a position ($R_n$, $\Theta_n$, $\Phi_n$), where $R_n$, $\Theta_n$, and $\Phi_n$ are the spherical polar coordinates of the acceptor relative to the donor and

$$\begin{aligned}t_{-(q_1+q_2)}^{(k_1+k_2)} &= (-1)^{k_2+q_1+q_2} \\ &\times \left[\frac{(k_1+k_2+q_1+q_2)!(k_1+k_2-q_1-q_2)!}{(k_1+q_1)!(k_1-q_1)!(k_2+q_2)!(k_2-q_2)!}\right]^{1/2} .\end{aligned} \tag{6}$$

The $k_1 = 0$ and $k_2 = 0$ term denotes the constant monopolar term. The first term in the expansion contributing to the energy-transfer process comes from the $k_1 = 1$ and $k_2 = 1$ term which contains the ED–ED interaction for both ions, $k_1 = 1$ and $k_2 = 2$ corresponds to an ED transition at the donor site accompanied by an EQ transition at the acceptor, and $k_1 = k_2 = 2$ represents the EQ–EQ interaction. Higher-order multipole–multipole interaction is very unlikely to give rise to the energy-transfer process and will therefore not be considered in this paper.

## 3 The geometric factor for multipole–multipole interaction

For acceptors at distances $R_n$ Eq. (2) may be summarized as

$$k_n^{\mathrm{CR}} = \sum_{s,p} G_n^{s_p} \frac{\alpha_{s_p}}{R_n^{s_p}} \ , \tag{7}$$

where the summation is over all the individual energy-transfer processes determined by the value of $s_p$ occurring at a specific donor ion each with a coupling parameter $\alpha_{s_p}$. $G_n^{s_p}$ is a geometric factor describing the angular dependence of the interaction between the donor transition multipole and the acceptor transition multipole.

With the multipole–multipole interaction given in Eq. (3) the perturbation matrix elements of Eq. (2) become

$$\begin{aligned}\left|\langle DA'|\hat{\mathrm{H}}_n|D'A\rangle\right|^2 &= \frac{e^4}{(4\pi\varepsilon_0\varepsilon_n)^2 R_n^{s_p}} \sum_{i,j} \left|\mu_{D'D}^i\right|^2 \left|\mu_{AA'}^j\right|^2 \\ &\times \sum_{q_1,q_2} \left|t_{-(q_1+q_2)}^{(k_1+k_2)}\right|^2 C_{-(q_1+q_2)}^{(k_1+k_2)} \\ &(\Theta_n, \Phi_n) C_{-(q_1+q_2)}^{(k_1+k_2)^*}(\Theta_n, \Phi_n)\end{aligned} \tag{8}$$

where the quantities $t_{-(q_1+q_2)}^{(k_1+k_2)}$ are calculated using Eq. (6). $\mu_{D'D}^i$ is the $i$th component of the transition multipole moment between the electronic states $D'$ and $D$ of the donor with a similar notation for the acceptor. The geometric factor may then be defined as

$$\begin{aligned}G_n^{s_p} &= \frac{1}{g_{\mathrm{D}} g_{\mathrm{A}}} \sum_{q_1,q_2} \left|t_{-(q_1+q_2)}^{(k_1+k_2)}\right|^2 C_{-(q_1+q_2)}^{(k_1+k_2)}(\Theta_n, \Phi_n) \\ &\times C_{-(q_1+q_2)}^{(k_1+k_2)^*}(\Theta_n, \Phi_n) \ ,\end{aligned} \tag{9}$$

where $g_{\mathrm{D}}$ and $g_{\mathrm{A}}$ are the degeneracies of the irreducible representations involved in the multipolar interaction such that $\left|\mu_{D'D}^i\right|^2 = |\mu_{D'D}|^2 \cdot (g_{\mathrm{D}})^{-1}$, etc. The multipole–multipole interaction in Eq. (8) then becomes

$$\left|\langle DA'|\hat{\mathrm{H}}_n|D'A\rangle\right|^2 = \frac{e^4 G_n^{s_p}}{(4\pi\varepsilon_0\varepsilon_n)^2 R_n^{s_p}} \sum |\mu_{D'D}|^2 |\mu_{AA'}|^2 \ . \tag{10}$$

The basis functions for the irreducible representations $E$, $T_1$, and $T_2$ of the octahedral point group used in our calculations are taken from Ref. [9].

### 3.1 *Dipole–dipole interaction*

The electric dipole operator transforms as the irreducible representation $T_1$ of the octahedral point group which has a threefold degeneracy and therefore the denominator in Eq. (9) becomes 9. For dipole–dipole interaction, $k_1 = k_2 = 1$ in Eq. (3) and the corresponding coupling coefficients $t_{-(q_1+q_2)}^{(2)}$ are given in Table 1. The geometric reduction factors for dipole–dipole coupling are independent of the shell number $n$ and are calculated to be 2/3.

### 3.2 *Dipole–quadrupole interaction*

Setting $k_1 = 1$ and $k_2 = 2$ in Eq. (3), the coupling coefficients $t_{-(q_1+q_2)}^{(3)}$ take the values given in Table 2. Notice that these quantities change their signs in the case of quadrupole–dipole interaction. In octahedral symmetry the EQ operator transforms as the direct sum of the

**Table 1.** Coupling coefficients for the dipole–dipole interaction in octahedral symmetry. $t^{(2)}_{\pm|q_1+q_2|}$ are the coefficients of $\left(C^{(2)}_{|q_1+q_2|} \pm C^{(2)}_{-|q_1+q_2|}\right)$, where $C^{(k)}_q$ are the standard Racah tensor operators

| $\Gamma_\mathrm{D} \rightarrow \Gamma_\mathrm{A}$ | $t^{(2)}_0$ | $t^{(2)}_{+1}$ | $t^{(2)}_{-1}$ | $t^{(2)}_{+2}$ | $t^{(2)}_{-2}$ |
|---|---|---|---|---|---|
| $T_1\alpha \rightarrow T_1\alpha$ | 1 | 0 | 0 | $-\sqrt{3/2}$ | 0 |
| $T_1\alpha \rightarrow T_1\beta$ | 0 | 0 | 0 | 0 | $i\sqrt{3/2}$ |
| $T_1\alpha \rightarrow T_1\gamma$ | 0 | 0 | $\sqrt{3/2}$ | 0 | 0 |
| $T_1\beta \rightarrow T_1\alpha$ | 0 | 0 | 0 | 0 | $i\sqrt{3/2}$ |
| $T_1\beta \rightarrow T_1\beta$ | 1 | 0 | 0 | $\sqrt{3/2}$ | 0 |
| $T_1\beta \rightarrow T_1\gamma$ | 0 | $-i\sqrt{3/2}$ | 0 | 0 | 0 |
| $T_1\gamma \rightarrow T_1\alpha$ | 0 | 0 | $\sqrt{3/2}$ | 0 | 0 |
| $T_1\gamma \rightarrow T_1\beta$ | 0 | $-i\sqrt{3/2}$ | 0 | 0 | 0 |
| $T_1\gamma \rightarrow T_1\gamma$ | −2 | 0 | 0 | 0 | 0 |

**Table 2.** Coupling coefficients for the dipole–quadrupole interaction in octahedral symmetry. $t^{(3)}_{\pm|q_1+q_2|}$ are the coefficients of $\left(C^{(3)}_{|q_1+q_2|} \pm C^{(3)}_{-|q_1+q_2|}\right)$, where $t^{(3)}_{\pm|q_1+q_2|} = -t^{(3)}_{\pm|q_1+q_2|}$ for quadrupole–dipole interaction

| $\Gamma_\mathrm{D} \rightarrow \Gamma_\mathrm{A}$ | $t^{(3)}_0$ | $t^{(3)}_{+1}$ | $t^{(3)}_{-1}$ | $t^{(3)}_{+2}$ | $t^{(3)}_{-2}$ | $t^{(3)}_{+3}$ | $t^{(3)}_{-3}$ |
|---|---|---|---|---|---|---|---|
| $T_1\alpha \rightarrow E\theta$ | 0 | 0 | $-\sqrt{3}$ | 0 | 0 | 0 | 0 |
| $T_1\alpha \rightarrow E\varepsilon$ | 0 | 0 | $1/2$ | 0 | 0 | 0 | $-\sqrt{15}/2$ |
| $T_1\alpha \rightarrow \mathrm{T}_2\xi$ | 0 | $-i/2$ | 0 | 0 | 0 | $i\sqrt{15}/2$ | 0 |
| $T_1\alpha \rightarrow \mathrm{T}_2\eta$ | $-\sqrt{3}$ | 0 | 0 | $\sqrt{10}/2$ | 0 | 0 | 0 |
| $T_1\alpha \rightarrow \mathrm{T}_2\zeta$ | 0 | 0 | 0 | 0 | $-i\sqrt{10}/2$ | 0 | 0 |
| $T_1\beta \rightarrow E\theta$ | 0 | $i\sqrt{3}$ | 0 | 0 | 0 | 0 | 0 |
| $T_1\beta \rightarrow E\varepsilon$ | 0 | $i/2$ | 0 | 0 | 0 | $i\sqrt{15}/2$ | 0 |
| $T_1\beta \rightarrow \mathrm{T}_2\xi$ | 0 | 0 | $1/2$ | 0 | 0 | 0 | $\sqrt{15}/2$ |
| $T_1\beta \rightarrow \mathrm{T}_2\eta$ | 0 | 0 | 0 | 0 | $-i\sqrt{10}/2$ | 0 | 0 |
| $T_1\beta \rightarrow \mathrm{T}_2\zeta$ | −1 | 0 | 0 | $-\sqrt{10}/2$ | 0 | 0 | 0 |
| $T_1\gamma \rightarrow E\theta$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 |
| $T_1\gamma \rightarrow E\varepsilon$ | 0 | 0 | 0 | $\sqrt{10}/2$ | 0 | 0 | 0 |
| $T_1\gamma \rightarrow T_2\xi$ | 0 | 0 | 0 | 0 | $-i\sqrt{10}/2$ | 0 | 0 |
| $T_1\gamma \rightarrow T_2\eta$ | 0 | 0 | −2 | 0 | 0 | 0 | 0 |
| $T_1\gamma \rightarrow \mathrm{T}_2\zeta$ | 0 | $2i$ | 0 | 0 | 0 | 0 | 0 |

**Table 3.** Geometric factors for dipole–quadrupole interaction among donor and acceptor ions. A typical set of spherical polar co–ordinates for acceptor sites in shells $n = 1$–10 is given. The maximum number of acceptor sites, $N_n$, is calculated by the permutation of positive and negative values of the corresponding Cartesian coordinates

| $n$ | $R_n/a_0$ | $N_n$ | $\Theta_n/\pi$ | $\Phi_n/\pi$ | $T_1 \leftrightarrow E$ | $T_1 \leftrightarrow T_2$ | $T_1 \leftrightarrow E \oplus T_2$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.707 | 12 | 0.5 | 0.25 | 0.3500 | 0.6500 | 1.000 |
| 2 | 1.000 | 6 | 0.5 | 0 | 0.6000 | 0.4000 | 1.000 |
| 3 | 1.225 | 24 | 0.3661 | 0.1476 | 0.3500 | 0.6500 | 1.000 |
| 4 | 1.414 | 12 | 0.5 | 0.25 | 0.3500 | 0.6500 | 1.000 |
| 5 | 1.581 | 24 | 0.5 | 0.1024 | 0.5100 | 0.4900 | 1.000 |
| 6 | 1.732 | 8 | 0.3041 | 0.25 | 0.2667 | 0.7333 | 1.000 |
| 7 | 1.871 | 48 | 0.3205 | 0.1024 | 0.3500 | 0.6500 | 1.000 |
| 8 | 2.000 | 6 | 0.5 | 0 | 0.6000 | 0.4000 | 1.000 |
| 9 | 2.121 | 12 | 0.5 | 0.25 | 0.3500 | 0.6500 | 1.000 |
|  |  | 24 | 0.4243 | 0.0780 | 0.4981 | 0.5019 | 1.000 |
| 10 | 2.236 | 24 | 0.3524 | 0 | 0.4400 | 0.5600 | 1.000 |

irreps $E$ and $T_2$. Depending on the selection rules for EQ transitions three different components may add to the dipole–quadrupole coupling, $T_1 \rightarrow E$, $T_1 \rightarrow T_2$, and $T_1 \rightarrow E \oplus T_2$. The corresponding geometric factors are given in Table 3 for dipole–quadrupole interaction between the donor ion and acceptors in shells $n = 1 - 10$. We note that in the ninth shell two types of acceptors appear at a distance $R_9 = 2.121 \times a_0$, and occur at different angles relative to the donor. If both $T_1 \rightarrow E$ and $T_1 \rightarrow T_2$ coupling are allowed the geometric factor becomes independent of $n$.

### *3.3 Quadrupole–quadrupole interaction*

Six different components contribute to the quadrupole–quadrupole interaction between donor and acceptor ions with $k_1 = k_2 = 2$ in Eq. (3), $E \leftrightarrow E$, $E \leftrightarrow T_2$, $E \leftrightarrow E \oplus T_2$, $T_2 \leftrightarrow T_2$, $T_2 \leftrightarrow E \oplus T_2$, and $E \oplus T_2 \leftrightarrow E \oplus T_2$. The coefficients $t^{(4)}_{-(q_1+q_2)}$ are given in Table 4 and the geometric factors for the first ten acceptor shells are given in Table 5. We note that for the last case these factors are again independent of $n$ and are calculated to be 14/5.

**Table 4.** Coupling coefficients for the quadrupole–quadrupole interaction in octahedral symmetry. $t^{(4)}_{\pm|q_1+q_2|}$ are the coefficients of $\left(C^{(4)}_{|q_1+q_2|} \pm C^{(4)}_{-|q_1+q_2|}\right)$

| $\Gamma_D \rightarrow \Gamma_A$ | $t^{(4)}_0$ | $t^{(4)}_{+1}$ | $t^{(4)}_{-1}$ | $t^{(4)}_{+2}$ | $t^{(4)}_{-2}$ | $t^{(4)}_{+3}$ | $t^{(4)}_{-3}$ | $t^{(4)}_{+4}$ | $t^{(4)}_{-4}$ |
|---|---|---|---|---|---|---|---|---|---|
| $E\theta \rightarrow E\theta$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{70}/2$ | 0 |
| $E\theta \rightarrow E\varepsilon$ | 0 | 0 | 0 | $\sqrt{30}/2$ | 0 | 0 | 0 | 0 | 0 |
| $E\theta \rightarrow T_2\xi$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-i\sqrt{70}/2$ |
| $E\theta \rightarrow T_2\eta$ | 0 | 0 | $\sqrt{5}/2$ | 0 | 0 | 0 | $-\sqrt{35}/2$ | 0 | 0 |
| $E\theta \rightarrow T_2\zeta$ | 0 | $i\sqrt{5}/2$ | 0 | 0 | 0 | $i\sqrt{35}/2$ | 0 | 0 | 0 |
| $E\varepsilon \rightarrow E\theta$ | 0 | 0 | 0 | $\sqrt{30}/2$ | 0 | 0 | 0 | 0 | 0 |
| $E\varepsilon \rightarrow E\varepsilon$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $E\varepsilon \rightarrow T_2\xi$ | 0 | 0 | 0 | 0 | $-i\sqrt{30}/2$ | 0 | 0 | 0 | 0 |
| $E\varepsilon \rightarrow T_2\eta$ | 0 | 0 | $-\sqrt{15}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $E\varepsilon \rightarrow T_2\zeta$ | 0 | $i\sqrt{15}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $T_2\xi \rightarrow E\theta$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-i\sqrt{70}/2$ |
| $T_2\xi \rightarrow E\varepsilon$ | 0 | 0 | 0 | 0 | $-i\sqrt{30}/2$ | 0 | 0 | 0 | 0 |
| $T_2\xi \rightarrow T_2\xi$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | $-\sqrt{70}/2$ | 0 |
| $T_2\xi \rightarrow T_2\eta$ | 0 | $-i\sqrt{5}/2$ | 0 | 0 | 0 | $i\sqrt{35}/2$ | 0 | 0 | 0 |
| $T_2\xi \rightarrow T_2\zeta$ | 0 | 0 | $\sqrt{5}/2$ | 0 | 0 | 0 | $\sqrt{35}/2$ | 0 | 0 |
| $T_2\eta \rightarrow E\theta$ | 0 | 0 | $\sqrt{5}/2$ | 0 | 0 | 0 | $-\sqrt{35}/2$ | 0 | 0 |
| $T_2\eta \rightarrow E\varepsilon$ | 0 | 0 | $-\sqrt{15}$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $T_2\eta \rightarrow T_2\xi$ | 0 | $-i\sqrt{5}/2$ | 0 | 0 | 0 | $i\sqrt{35}/2$ | 0 | 0 | 0 |
| $T_2\eta \rightarrow T_2\eta$ | −4 | 0 | 0 | $\sqrt{10}$ | 0 | 0 | 0 | 0 | 0 |
| $T_2\eta \rightarrow T_2\zeta$ | 0 | 0 | 0 | 0 | $-i\sqrt{10}$ | 0 | 0 | 0 | 0 |
| $T_2\zeta \rightarrow E\theta$ | 0 | $i\sqrt{5}/2$ | 0 | 0 | 0 | $i\sqrt{35}/2$ | 0 | 0 | 0 |
| $T_2\zeta \rightarrow E\varepsilon$ | 0 | $i\sqrt{15}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $T_2\zeta \rightarrow T_2\xi$ | 0 | 0 | $\sqrt{5}/2$ | 0 | 0 | 0 | $\sqrt{35}/2$ | 0 | 0 |
| $T_2\zeta \rightarrow T_2\eta$ | 0 | 0 | 0 | 0 | $-i\sqrt{10}$ | 0 | 0 | 0 | 0 |
| $T_2\zeta \rightarrow T_2\zeta$ | −4 | 0 | 0 | $-\sqrt{10}$ | 0 | 0 | 0 | 0 | 0 |

**Table 5.** Geometric factors for quadrupole–quadrupole interaction among donor and acceptor ions. A typical set of spherical polar coordinates for acceptor sites in shells $n = 1$–10 is given. The maximum number of acceptor sites, $N_n$, is calculated by the permutation of positive and negative values of the corresponding Cartesian coordinates

| $N$ | $R_n/a_0$ | $N_n$ | $\Theta_n/\pi$ | $\Phi_n/\pi$ | $E \leftrightarrow E$ | $E \leftrightarrow T_2$ | $E \leftrightarrow E \oplus T_2$ | $T_2 \leftrightarrow T_2$ | $T_2 \leftrightarrow E \oplus T_2$ | $E \oplus T_2 \leftrightarrow E \oplus T_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.707 | 12 | 0.5 | 0.25 | 0.8425 | 0.1875 | 1.030 | 1.583 | 1.770 | 2.800 |
| 2 | 1.000 | 6 | 0.5 | 0 | 1.480 | 0 | 1.480 | 1.320 | 1.320 | 2.800 |
| 3 | 1.225 | 24 | 0.3661 | 0.1476 | 0.0647 | 0.9653 | 1.030 | 0.8047 | 1.770 | 2.800 |
| 4 | 1.414 | 12 | 0.5 | 0.25 | 0.8425 | 0.1875 | 1.030 | 1.583 | 1.770 | 2.800 |
| 5 | 1.581 | 24 | 0.5 | 0.1024 | 0.5449 | 0.7731 | 1.318 | 0.7089 | 1.482 | 2.800 |
| 6 | 1.732 | 8 | 0.3041 | 0.25 | 0.4356 | 0.4444 | 0.8800 | 1.476 | 1.920 | 2.800 |
| 7 | 1.871 | 48 | 0.3205 | 0.1024 | 0.2915 | 0.7385 | 1.030 | 1.032 | 1.770 | 2.800 |
| 8 | 2.000 | 6 | 0.5 | 0 | 1.480 | 0 | 1.480 | 1.320 | 1.320 | 2.800 |
| 9 | 2.121 | 12 | 0.5 | 0.25 | 0.8425 | 0.1875 | 1.030 | 1.583 | 1.770 | 2.800 |
|  |  | 24 | 0.4243 | 0.0780 | 0.3657 | 0.9310 | 1.297 | 0.5723 | 1.503 | 2.800 |
| 10 | 2.236 | 24 | 0.3524 | 0 | 0.3664 | 0.8256 | 1.192 | 0.7824 | 1.608 | 2.800 |

## 4 Conclusions

The calculation of the geometric factors for multipole–multipole interactions up to quadrupole–quadrupole has been presented in detail. Numerical results up to $n = 10$ have been tabulated although only the lower values of $n$ are likely to be important in physical systems. The geometric factors differ from shell to shell except for dipole–dipole interaction or when the separation between the emissive levels is small compared to $kT$. Otherwise these geometric factors are sufficiently small to require their inclusion in practical calculations of excitation decay and luminescence efficiency.

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