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Potential integrals in kubic harmonic basis set

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Abstract. The expansion of either crystal-field or electron–electron potentials usually makes use of the addition theorem for spherical harmonics. Hence, in order to calculate matrix elements of the potential taken between electronic states, one must perform integrals of the product of three spherical harmonics. Tables are readily available for these integrals. However, it is often more convenient to express the electronic states in terms of real functions, so-called kubic harmonics, and the addition theorem can be rewritten in terms of kubic harmonics. This results in the necessity of calculating integrals that are the products of three kubic harmonics. We tabulate here the required integrals. We have found these tables useful and believe that they may be useful to others.

1. Introduction

It is often easier to express crystal-field matrix elements using a kubic harmonic basis set rather than the usual spherical harmonics. (The term kubic harmonic was first coined by Von der Lage and Bethe [1].) This is particularly true for low-symmetry crystal fields. This kind of representation also allows for insight and physical interpretation of the crystal-field parameters that is not afforded with spherical harmonic representations [2–4]. A problem arises however in the computation of the full Hamiltonian in that the electron–electron interaction is almost always calculated using a spherical harmonic representation for the electronic states. This necessitates a change in basis in order to calculate the crystal-field matrix elements. While this is not excessively difficult, it is an extra step. An alternative would be to employ a kubic harmonic basis from the outset. Hence, we need to calculate the electron–electron interaction in terms of kubic harmonics.

The interaction between electrons or the interaction between an electron and a neighbouring ion involves the expansion of $1/r_{ij}$; cf [6] and [5]. This is nicely handled using the generating function for the Legendre polynomials. The Legendre polynomial (P_k) is then expanded using the addition theorem for spherical harmonics (Y_{km})

$$P_k(\cos\omega) = \left(\frac{4\pi}{2k+1}\right) \sum_{m=-k}^{k} Y_{km}(\theta_i, \phi_i) Y^*_{km}(\theta_j, \phi_j) \qquad (1)$$

where ω is the angle between (θ_i, ϕ_i) and (θ_j, ϕ_j), which along with r_i and r_j give the positions of the two interacting charges. The sum of products of spherical harmonics, however, can be rewritten as a sum of products of kubic harmonics (KH_{kq}) [5]

$$P_k(\cos\omega) = \frac{1}{2k+1} \sum_q \mathrm{KH}_{kq}(x_i, y_i, z_i)\mathrm{KH}_{kq}(x_j, y_j, z_j). \qquad (2)$$

Table 1. Kubic harmonic operators (KH_{kq}) for $k = 0$–6 normalized to 4π. Each function must be divided by a factor of r^k, and is labelled according to its transformations under the rotation group of the cube. Further details are discussed in the text.

$k = 0(a_1)$	1
$k = 1(t_1)$	$\sqrt{3}z$
$k = 2(e_\theta)$	$\sqrt{5}/2(3z^2 - r^2)$
$k = 2(e_\epsilon)$	$\sqrt{15}/2(x^2 - y^2)$
$k = 2(t_{2\zeta})$	$\sqrt{15}xy$
$k = 3(a_2)$	$\sqrt{105}xyz$
$k = 3(t_{1z})$	$\sqrt{7}/2z(5z^2 - 3r^2)$
$k = 3(t_{2\zeta})$	$\sqrt{105}/2z(x^2 - y^2)$
$k = 4(a_1)$	$\sqrt{21}/4(5(x^4 + y^4 + z^4) - 3r^4)$
$k = 4(e_\theta)$	$\sqrt{15}/2(7(z^4 - 1/2(x^4 + y^4)) - 6(z^2 - 1/2(x^2 + y^2))r^2)$
$k = 4(e_\epsilon)$	$3\sqrt{5}/4(7(x^4 - y^4) - 6(x^2 - y^2)r^2)$
$k = 4(t_{1z})$	$3\sqrt{35}/2xy(x^2 - y^2)$
$k = 4(t_{2\zeta})$	$3\sqrt{5}/2xy(7z^2 - r^2)$
$k = 5(e_\theta)$	$3\sqrt{385}/2xyz(x^2 - y^2)$
$k = 5(e_\epsilon)$	$-\sqrt{1155}/2xyz(3z^2 - r^2)$
$k = 5(t_{1z}^a)$	$\sqrt{11}/8(63z^5 - 70z^3r^2 + 15zr^4)$
$k = 5(t_{1z}^b)$	$3\sqrt{385}/8z(x^4 - 6x^2y^2 + y^4)$
$k = 5(t_{2\zeta})$	$\sqrt{1155}/4z(3z^2 - r^2)(x^2 - y^2)$
$k = 6(a_1)$	$\sqrt{26}/8(2r^6 - 21(x^2y^2 + y^2z^2 + z^2x^2)r^2 + 231x^2y^2z^2)$
$k = 6(a_2)$	$\sqrt{30\,030}/8(x^4y^2 + y^4z^2 + z^4x^2 - x^2y^4 - y^2z^4 - z^2x^4)$
$k = 6(e_\theta)$	$\sqrt{182}/4(11(z^6 - 1/2(x^6 + y^6)) - 15(z^4 - 1/2(x^4 + y^4))r^2 + 5(z^2 - 1/2(x^2 + y^2))r^4)$
$k = 6(e_\epsilon)$	$\sqrt{546}/8(11(x^6 - y^6) - 15(x^4 - y^4)r^2 + 5(x^2 - y^2)r^4)$
$k = 6(t_{1z})$	$3\sqrt{91}/4xy(11z^2 - r^2)(x^2 - y^2)$
$k = 6(t_{2\zeta}^a)$	$\sqrt{2730}/16xy(33z^4 - 18z^2r^2 + r^4)$
$k = 6(t_{2\zeta}^b)$	$\sqrt{6006}/16xy(3x^4 - 10x^2y^2 + 3y^4)$

This result follows because the kubic harmonics are real and can be obtained from the spherical harmonics for a given value of k through a unitary transform. We note, however, that while the spherical harmonics are normailized to unity, the kubic harmonics are normalized to 4π; hence the absence of 4π from the numerator of equation (2). In order to be explicit in our definitions, we show in table 1 the kubic harmonics up to $k = 6$ [1]. (Whereas γ_1 and γ_2 in [1] transform as e_θ and e_ϵ, repectively, γ_1' and γ_2' transform as $-e_\epsilon$ and e_θ, repectively. The only error we have found is in α_8 in which the coefficient of ρ^8 should be $-1/3$, not $-1/6$.) The $x(\xi)$ and $y(\eta)$ kubic harmonics within the $t_1(t_2)$ manifolds are simply obtained by permuting the variables x, y and z in the corresponding $z(\zeta)$ kubic harmonic. We note that each of these functions must be divided by a factor of r^k and that the functions are labelled according to the irreducible representations of the rotation group of the cube, not of the tetrahedron.

In order to calculate matrix elements of the potential using a kubic harmonic basis set for the electrons, we need to determine the integrals of the product of three kubic harmonics

$$c_{kq}(lm, l'm') = \frac{1}{4\pi} \oint_{us} KH_{lm}(x, y, z) KH_{kq}(x, y, z) KH_{l'm'}(x, y, z)\, dS \qquad (3)$$

where the integral is over the surface of the unit sphere. (The factor of $(4\pi)^{-1}$ makes the KH_{lm} and $KH_{l'm'}$ normalized electronic states.) Table 2 tabulates the quantities $c_{kq}(lm, l'm')$ which are unchanged by any permutations of (kq), (lm) and $(l'm')$. (We have found an error in the overall constant that multiplies the factors given in the table of [6] for the $k = 5$ component of the d–f interaction. We have determined this overall factor to be $\sqrt{35}/231$.) We note that while there is only one possible Y_{kq}, for k fixed, which results in a non-zero integral when taken between Y_{lm} and $Y_{l'm'}$, there may be more than one kubic harmonic KH_{kq} that results in a non-zero integral when taken between kubic harmonics KH_{lm} and $\mathrm{KH}_{l'm'}$. Of course, the usual triangle inequality holds on the values of k, $|l - l'| \leqslant k \leqslant l + l'$, and the sum $k + l + l'$ must be even. The particular kubic harmonic operator from within a t_1 or t_2 manifold that couples the kubic harmonic wavefunctions KH_{lm} and $\mathrm{KH}_{l'm'}$ can be determined from the group coupling coefficients, like those given in appendix 2 of [5] or those of [7]. Briefly summarizing these tables, kubic harmonics of t_{1z} symmetry couple $a_{1(2)}$ states to $t_{1z(2\zeta)}$ states as well as $\mathrm{e}_{\theta(\epsilon)}$ states to t_{1z} states, and $t_{1x(1y)}$ states to $t_{2\eta(2\xi)}$ states. Also, kubic harmonics of $t_{2\zeta}$ symmetry couple $a_{1(2)}$ states to $t_{2\zeta(1z)}$ states as well as $\mathrm{e}_{\theta(\epsilon)}$ states to $t_{2\zeta}$ states, and $t_{1x(2\xi)}$ states to $t_{1y(2\eta)}$ states. The coupling properties of the other t_1 and t_2 states can be obtained from cyclic permutations of $x, y, z(\xi, \eta, \zeta)$ in these rules.

2. Discussion

In this section, we give an example of the application of the tables to demonstrate how easily they can be used. We determine the diagonal matrix element of the electron–electron interaction within the $(\xi\eta\bar{\theta})$ Slater determinant from the d^3 configuration. (The bar over the θ state indicates the spin-down state.) The electron–electron interaction $E_{\mathrm{e–e}}$ in this instance is composed of three direct Coulomb integrals and one exchange integral

$$E_{\mathrm{e–e}} = \langle\xi\eta||\xi\eta\rangle + \langle\xi\theta||\xi\theta\rangle + \langle\eta\theta||\eta\theta\rangle - \langle\xi\eta||\eta\xi\rangle \tag{4}$$

where

$$\langle\psi_i\psi_j||\psi_m\psi_n\rangle = \int \psi_i^*(1)\psi_j^*(2)1/r_{12}\psi_m(1)\psi_n(2)\,\mathrm{d}^3r_1\,\mathrm{d}^3r_2. \tag{5}$$

Expanding $1/r_{12}$ using the addition theorem for kubic harmonics and using the definition of $c_{kq}(lm, l'm')$ in equation (3), $\langle\xi\eta||\xi\eta\rangle$ is expanded as

$$\begin{aligned}\langle\xi\eta||\xi\eta\rangle &= \sum_{k=0,2,4} \frac{F^k}{2k+1} \sum_q c_{kq}(d_\xi, d_\xi)c_{kq}(d_\eta, d_\eta)\\ &= [F^0 + \tfrac{1}{5}\tfrac{5-15}{49}F^2 + \tfrac{1}{9}\tfrac{84+60-180}{441}F^4]\end{aligned} \tag{6}$$

where the $c_{kq}(lm, l'm')$ have been taken from table 2 and the F^k are the radial integrals associated with the kth term in the expansion of $1/r_{12}$; cf [6]. In a similar fashion, we also find that

$$\begin{aligned}\langle\xi\theta||\xi\theta\rangle &= [F^0 + \tfrac{1}{5}\tfrac{10}{49}F^2 + \tfrac{1}{9}\tfrac{-126-90}{441}F^4]\\ \langle\eta\theta||\eta\theta\rangle &= [F^0 + \tfrac{1}{5}\tfrac{10}{49}F^2 + \tfrac{1}{9}\tfrac{-126-90}{441}F^4]\\ \langle\xi\eta||\eta\xi\rangle &= [\tfrac{1}{5}\tfrac{15}{49}F^2 + \tfrac{1}{9}\tfrac{180}{441}F^4].\end{aligned} \tag{7}$$

The use of kubic harmonics in problems relating to the crystal-field interaction is far easier than the use of spherical harmonics [2–4]. The expansion of the crystal field in terms of the irreducible representations of the cubic group can be done by simply examining the geometrical configuration of the atoms giving rise to the crystal field. Often, this geometrical configuration of atoms can be described as a reduction from (a distortion of) cubic symmetry. The operators found in the crystal-field interaction are simply the basis functions of the irreducible representations that possess the same symmetry (that transform in the same manner under the cubic group symmetry operators) as the distortions used to reduce the symmetry from

Table 2. Values for the integrals of the products of three kubic harmonics, $c_{kq}(lm, l'm')$.

ψ_i	ψ_j	$k = 0(a_1)$	$k = 2(\mathrm{e}_\theta)$	$k = 2(\mathrm{e}_\epsilon)$	$k = 2(t_2)$
s	s	1			
p_x	p_x	1	$-\sqrt{5}/5$	$\sqrt{15}/5$	0
p_x	p_y	0	0	0	$\sqrt{15}/5$
p_x	p_z	0	0	0	$\sqrt{15}/5$
p_y	p_y	1	$-\sqrt{5}/5$	$-\sqrt{15}/5$	0
p_y	p_z	0	0	0	$\sqrt{15}/5$
p_z	p_z	1	$2\sqrt{5}/5$	0	0
d_ξ	d_ξ	1	$\sqrt{5}/7$	$-\sqrt{15}/7$	0
d_ξ	d_η	0	0	0	$\sqrt{15}/7$
d_ξ	d_ζ	0	0	0	$\sqrt{15}/7$
d_ξ	d_θ	0	0	0	$\sqrt{5}/7$
d_ξ	d_ϵ	0	0	0	$-\sqrt{15}/7$
d_η	d_η	1	$\sqrt{5}/7$	$\sqrt{15}/7$	0
d_η	d_ζ	0	0	0	$\sqrt{15}/7$
d_η	d_θ	0	0	0	$\sqrt{5}/7$
d_η	d_ϵ	0	0	0	$\sqrt{15}/7$
d_ζ	d_ζ	1	$-2\sqrt{5}/7$	0	0
d_ζ	d_θ	0	0	0	$-2\sqrt{5}/7$
d_ζ	d_ϵ	0	0	0	0
d_θ	d_θ	1	$2\sqrt{5}/7$	0	0
d_θ	d_ϵ	0	0	$-2\sqrt{5}/7$	0
d_ϵ	d_ϵ	1	$-2\sqrt{5}/7$	0	0
f_a	f_a	1	0	0	0
f_a	f_x	0	0	0	$-2/3$
f_a	f_y	0	0	0	$-2/3$
f_a	f_z	0	0	0	$-2/3$
f_a	f_ξ	0	0	0	0
f_a	f_η	0	0	0	0
f_a	f_ζ	0	0	0	0
f_x	f_x	1	$-2\sqrt{5}/15$	$2\sqrt{15}/15$	0
f_x	f_y	0	0	0	$-\sqrt{15}/30$
f_x	f_z	0	0	0	$-\sqrt{15}/30$
f_x	f_ξ	0	$\sqrt{3}/3$	$1/3$	0
f_x	f_η	0	0	0	$-1/6$
f_x	f_ζ	0	0	0	$1/6$
f_y	f_y	1	$-2\sqrt{5}/15$	$-2\sqrt{15}/15$	0
f_y	f_z	0	0	0	$-\sqrt{15}/30$
f_y	f_ξ	0	0	0	$1/6$
f_y	f_η	0	$-\sqrt{3}/3$	$1/3$	0
f_y	f_ζ	0	0	0	$-1/6$
f_z	f_z	1	$4\sqrt{5}/15$	0	0
f_z	f_ξ	0	0	0	$-1/6$
f_z	f_η	0	0	0	$1/6$
f_z	f_ζ	0	0	$-2/3$	0
f_ξ	f_ξ	1	0	0	0
f_ξ	f_η	0	0	0	$-\sqrt{15}/6$
f_ξ	f_ζ	0	0	0	$-\sqrt{15}/6$

Table 2. (Continued)

ψ_i	ψ_j	$k=0(a_1)$	$k=2(e_\theta)$	$k=2(e_\epsilon)$	$k=2(t_2)$	
f_η	f_η	1	0	0	0	
f_η	f_ζ	0	0	0	$-\sqrt{15}/6$	
f_ζ	f_ζ	1	0	0	0	
ψ_i	ψ_j	$k=4(a_1)$	$k=4(e_\theta)$	$k=4(e_\epsilon)$	$k=4(t_1)$	$k=4(t_2)$
d_ξ	d_ξ	$-2\sqrt{21}/21$	$-2\sqrt{15}/21$	$2\sqrt{5}/7$	0	0
d_ξ	d_η	0	0	0	0	$2\sqrt{5}/7$
d_ξ	d_ζ	0	0	0	0	$2\sqrt{5}/7$
d_ξ	d_θ	0	0	0	$-\sqrt{105}/14$	$-\sqrt{15}/14$
d_ξ	d_ϵ	0	0	0	$-\sqrt{35}/14$	$3\sqrt{5}/14$
d_η	d_η	$-2\sqrt{21}/21$	$-2\sqrt{15}/21$	$-2\sqrt{5}/7$	0	0
d_η	d_ζ	0	0	0	0	$2\sqrt{5}/7$
d_η	d_θ	0	0	0	$\sqrt{105}/14$	$-\sqrt{15}/14$
d_η	d_ϵ	0	0	0	$-\sqrt{35}/14$	$-3\sqrt{5}/14$
d_ζ	d_ζ	$-2\sqrt{21}/21$	$4\sqrt{15}/21$	0	0	0
d_ζ	d_θ	0	0	0	0	$\sqrt{15}/7$
d_ζ	d_ϵ	0	0	0	$\sqrt{35}/7$	0
d_θ	d_θ	$\sqrt{21}/7$	$\sqrt{15}/7$	0	0	0
d_θ	d_ϵ	0	0	$-\sqrt{15}/7$	0	0
d_ϵ	d_ϵ	$\sqrt{21}/7$	$-\sqrt{15}/7$	0	0	0
f_a	f_a	$-2\sqrt{21}/11$	0	0	0	0
f_a	f_x	0	0	0	0	$-\sqrt{3}/11$
f_a	f_y	0	0	0	0	$-\sqrt{3}/11$
f_a	f_z	0	0	0	0	$-\sqrt{3}/11$
f_a	f_ξ	0	0	0	$\sqrt{35}/11$	0
f_a	f_η	0	0	0	$\sqrt{35}/11$	0
f_a	f_ζ	0	0	0	$\sqrt{35}/11$	0
f_x	f_x	$\sqrt{21}/11$	$-\sqrt{15}/22$	$3\sqrt{5}/22$	0	0
f_x	f_y	0	0	0	0	$3\sqrt{5}/11$
f_x	f_z	0	0	0	0	$3\sqrt{5}/11$
f_x	f_ξ	0	$-3/22$	$-\sqrt{3}/22$	0	0
f_x	f_η	0	0	0	$-\sqrt{21}/11$	$-2\sqrt{3}/11$
f_x	f_ζ	0	0	0	$-\sqrt{21}/11$	$2\sqrt{3}/11$
f_y	f_y	$\sqrt{21}/11$	$-\sqrt{15}/22$	$-3\sqrt{5}/22$	0	0
f_y	f_z	0	0	0	0	$3\sqrt{5}/11$
f_y	f_ξ	0	0	0	$-\sqrt{21}/11$	$2\sqrt{3}/11$
f_y	f_η	0	$3/22$	$-\sqrt{3}/22$	0	0
f_y	f_ζ	0	0	0	$-\sqrt{21}/11$	$-2\sqrt{3}/11$
f_z	f_z	$\sqrt{21}/11$	$\sqrt{15}/11$	0	0	0
f_z	f_ξ	0	0	0	$-\sqrt{21}/11$	$-2\sqrt{3}/11$
f_z	f_η	0	0	0	$-\sqrt{21}/11$	$2\sqrt{3}/11$
f_z	f_ζ	0	0	$\sqrt{3}/11$	0	0
f_ξ	f_ξ	$-\sqrt{21}/33$	$7\sqrt{15}/66$	$-7\sqrt{5}/22$	0	0
f_ξ	f_η	0	0	0	0	$\sqrt{5}/11$
f_ξ	f_ζ	0	0	0	0	$\sqrt{5}/11$
f_η	f_η	$-\sqrt{21}/33$	$7\sqrt{15}/66$	$7\sqrt{5}/22$	0	0

Table 2. (Continued)

ψ_i	ψ_j	$k=4(a_1)$	$k=4(e_\theta)$	$k=4(e_\epsilon)$	$k=4(t_1)$	$k=4(t_2)$
f_η	f_ζ	0	0	0	0	$\sqrt{5}/11$
f_ζ	f_ζ	$-\sqrt{21}/33$	$-7\sqrt{15}/33$	0	0	0

ψ_i	ψ_j	$k=6(a_1)$	$k=6(a_2)$	$k=6(e_\theta)$	$k=6(e_\epsilon)$
f_a	f_a	$20\sqrt{26}/143$	0	0	0
f_a	f_x	0	0	0	0
f_a	f_y	0	0	0	0
f_a	f_z	0	0	0	0
f_a	f_ξ	0	0	0	0
f_a	f_η	0	0	0	0
f_a	f_ζ	0	0	0	0
f_x	f_x	$25\sqrt{26}/429$	0	$-25\sqrt{182}/858$	$25\sqrt{546}/858$
f_x	f_y	0	0	0	0
f_x	f_z	0	0	0	0
f_x	f_ξ	0	$5\sqrt{2002}/429$	$-5\sqrt{2730}/858$	$-5\sqrt{910}/858$
f_x	f_η	0	0	0	0
f_x	f_ζ	0	0	0	0
f_y	f_y	$25\sqrt{26}/429$	0	$-25\sqrt{182}/858$	$-25\sqrt{546}/858$
f_y	f_z	0	0	0	0
f_y	f_ξ	0	0	0	0
f_y	f_η	0	$5\sqrt{2002}/429$	$5\sqrt{2730}/858$	$-5\sqrt{910}/858$
f_y	f_ζ	0	0	0	0
f_z	f_z	$25\sqrt{26}/429$	0	$25\sqrt{182}/429$	0
f_z	f_ξ	0	0	0	0
f_z	f_η	0	0	0	0
f_z	f_ζ	0	$5\sqrt{2002}/429$	0	$5\sqrt{910}/429$
f_ξ	f_ξ	$-15\sqrt{26}/143$	0	$-5\sqrt{182}/286$	$5\sqrt{546}/286$
f_ξ	f_η	0	0	0	0
f_ξ	f_ζ	0	0	0	0
f_η	f_η	$-15\sqrt{26}/143$	0	$-5\sqrt{182}/286$	$-5\sqrt{546}/286$
f_η	f_ζ	0	0	0	0
f_ζ	f_ζ	$-15\sqrt{26}/143$	0	$5\sqrt{182}/143$	0

ψ_i	ψ_j	$k=6(t_1)$	$k=6(t_2^a)$	$k=6(t_2^b)$
f_a	f_a	0	0	0
f_a	f_x	0	$20\sqrt{182}/429$	0
f_a	f_y	0	$20\sqrt{182}/429$	0
f_a	f_z	0	$20\sqrt{182}/429$	0
f_a	f_ξ	$10\sqrt{91}/143$	0	0
f_a	f_η	$10\sqrt{91}/143$	0	0
f_a	f_ζ	$10\sqrt{91}/143$	0	0
f_x	f_x	0	0	0
f_x	f_y	0	$5\sqrt{2730}/3432$	$-25\sqrt{6006}/3432$
f_x	f_z	0	$5\sqrt{2730}/3432$	$-25\sqrt{6006}/3432$
f_x	f_ξ	0	0	0
f_x	f_η	$5\sqrt{1365}/429$	$-5\sqrt{182}/264$	$-5\sqrt{10\,010}/1144$
f_x	f_ζ	$5\sqrt{1365}/429$	$5\sqrt{182}/264$	$5\sqrt{10\,010}/1144$
f_y	f_y	0	0	0
f_y	f_z	0	$5\sqrt{2730}/3432$	$-25\sqrt{6006}/3432$

Table 2. (Continued)

ψ_i	ψ_j	$k = 6(t_1)$	$k = 6(t_2^a)$	$k = 6(t_2^b)$
f_y	f_ξ	$5\sqrt{1365}/429$	$5\sqrt{182}/264$	$5\sqrt{10\,010}/1144$
f_y	f_η	0	0	0
f_y	f_ζ	$5\sqrt{1365}/429$	$-5\sqrt{182}/264$	$-5\sqrt{10\,010}/1144$
f_z	f_z	0	0	0
f_z	f_ξ	$5\sqrt{1365}/429$	$-5\sqrt{182}/264$	$-5\sqrt{10\,010}/1144$
f_z	f_η	$5\sqrt{1365}/429$	$5\sqrt{182}/264$	$5\sqrt{10\,010}/1144$
f_z	f_ζ	0	0	0
f_ξ	f_ξ	0	0	0
f_ξ	f_η	0	$-35\sqrt{2730}/3432$	$5\sqrt{6006}/1144$
f_ξ	f_ζ	0	$-35\sqrt{2730}/3432$	$5\sqrt{6006}/1144$
f_η	f_η	0	0	0
f_η	f_ζ	0	$-35\sqrt{2730}/3432$	$5\sqrt{6006}/1144$
f_ζ	f_ζ	0	0	0

ψ_i	ψ_j	$k = 2(e_\theta)$	$k = 2(e_\epsilon)$	$k = 2(t_2)$
s	d_ξ	0	0	1
s	d_η	0	0	1
s	d_ζ	0	0	1
s	d_θ	1	0	0
s	d_ϵ	0	1	0
p_x	f_a	0	0	$\sqrt{21}/7$
p_x	f_x	$-3\sqrt{105}/70$	$9\sqrt{35}/70$	0
p_x	f_y	0	0	$-3\sqrt{35}/35$
p_x	f_z	0	0	$-3\sqrt{35}/35$
p_x	f_ξ	$-3\sqrt{7}/14$	$-\sqrt{21}/14$	0
p_x	f_η	0	0	$-\sqrt{21}/7$
p_x	f_ζ	0	0	$\sqrt{21}/7$
p_y	f_a	0	0	$\sqrt{21}/7$
p_y	f_x	0	0	$-3\sqrt{35}/35$
p_y	f_y	$-3\sqrt{105}/70$	$-9\sqrt{35}/70$	0
p_y	f_z	0	0	$-3\sqrt{35}/35$
p_y	f_ξ	0	0	$\sqrt{21}/7$
p_y	f_η	$3\sqrt{7}/14$	$-\sqrt{21}/14$	0
p_y	f_ζ	0	0	$-\sqrt{21}/7$
p_z	f_a	0	0	$\sqrt{21}/7$
p_z	f_x	0	0	$-3\sqrt{35}/35$
p_z	f_y	0	0	$-3\sqrt{35}/35$
p_z	f_z	$3\sqrt{105}/35$	0	0
p_z	f_ξ	0	0	$-\sqrt{21}/7$
p_z	f_η	0	0	$\sqrt{21}/7$
p_z	f_ζ	0	$\sqrt{21}/7$	0

ψ_i	ψ_j	$k = 4(a_1)$	$k = 4(e_\theta)$	$k = 4(e_\epsilon)$	$k = 4(t_1)$	$k = 4(t_2)$
p_x	f_a	0	0	0	0	$2\sqrt{7}/7$
p_x	f_x	2/3	$-\sqrt{35}/21$	$\sqrt{105}/21$	0	0
p_x	f_y	0	0	0	$-\sqrt{15}/6$	$-\sqrt{105}/42$
p_x	f_z	0	0	0	$\sqrt{15}/6$	$-\sqrt{105}/42$

Table 2. (Continued)

ψ_i	ψ_j	$k=4(a_1)$	$k=4(e_\theta)$	$k=4(e_\epsilon)$	$k=4(t_1)$	$k=4(t_2)$
p_x	f_ξ	0	$\sqrt{21}/7$	$\sqrt{7}/7$	0	0
p_x	f_η	0	0	0	$-1/2$	$3\sqrt{7}/14$
p_x	f_ζ	0	0	0	$-1/2$	$-3\sqrt{7}/14$
p_y	f_a	0	0	0	0	$2\sqrt{7}/7$
p_y	f_x	0	0	0	$\sqrt{15}/6$	$-\sqrt{105}/42$
p_y	f_y	$2/3$	$-\sqrt{35}/21$	$-\sqrt{105}/21$	0	0
p_y	f_z	0	0	0	$-\sqrt{15}/6$	$-\sqrt{105}/42$
p_y	f_ξ	0	0	0	$-1/2$	$-3\sqrt{7}/14$
p_y	f_η	0	$-\sqrt{21}/7$	$\sqrt{7}/7$	0	0
p_y	f_ζ	0	0	0	$-1/2$	$3\sqrt{7}/14$
p_z	f_a	0	0	0	0	$2\sqrt{7}/7$
p_z	f_x	0	0	0	$-\sqrt{15}/6$	$-\sqrt{105}/42$
p_z	f_y	0	0	0	$\sqrt{15}/6$	$-\sqrt{105}/42$
p_z	f_z	$2/3$	$2\sqrt{35}/21$	0	0	0
p_z	f_ξ	0	0	0	$-1/2$	$3\sqrt{7}/14$
p_z	f_η	0	0	0	$-1/2$	$-3\sqrt{7}/14$
p_z	f_ζ	0	0	$-2\sqrt{7}/7$	0	0

ψ_i	ψ_j	$k=1(t_1)$	$k=3(a_2)$	$k=3(t_1)$	$k=3(t_2)$
s	p_x	1			
s	p_y	1			
s	p_z	1			
s	f_a		1	0	0
s	f_x		0	1	0
s	f_y		0	1	0
s	f_z		0	1	0
s	f_ξ		0	0	1
s	f_η		0	0	1
s	f_ζ		0	0	1
p_x	d_ξ	0	$\sqrt{21}/7$	0	0
p_x	d_η	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$\sqrt{21}/7$
p_x	d_ζ	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$-\sqrt{21}/7$
p_x	d_θ	$-\sqrt{5}/5$	0	$-3\sqrt{105}/70$	$-3\sqrt{7}/14$
p_x	d_ϵ	$\sqrt{15}/5$	0	$9\sqrt{35}/70$	$-\sqrt{21}/14$
p_y	d_ξ	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$-\sqrt{21}/7$
p_y	d_η	0	$\sqrt{21}/7$	0	0
p_y	d_ζ	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$\sqrt{21}/7$
p_y	d_θ	$-\sqrt{5}/5$	0	$-3\sqrt{105}/70$	$3\sqrt{7}/14$
p_y	d_ϵ	$-\sqrt{15}/5$	0	$-9\sqrt{35}/70$	$-\sqrt{21}/14$
p_z	d_ξ	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$\sqrt{21}/7$
p_z	d_η	$\sqrt{15}/5$	0	$-3\sqrt{35}/35$	$-\sqrt{21}/7$
p_z	d_ζ	0	$\sqrt{21}/7$	0	0
p_z	d_θ	$2\sqrt{5}/5$	0	$3\sqrt{105}/35$	0
p_z	d_ϵ	0	0	0	$\sqrt{21}/7$
d_ξ	f_a	$\sqrt{21}/7$	0	$-2/3$	0
d_ξ	f_x	0	$-2/3$	0	0
d_ξ	f_y	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$-1/6$

Table 2. (Continued)

ψ_i	ψ_j	$k=1(t_1)$	$k=3(a_2)$	$k=3(t_1)$	$k=3(t_2)$	
d_ξ	f_z	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$1/6$	
d_ξ	f_ξ	0	0	0	0	
d_ξ	f_η	$\sqrt{21}/7$	0	$1/6$	$-\sqrt{15}/6$	
d_ξ	f_ζ	$-\sqrt{21}/7$	0	$-1/6$	$-\sqrt{15}/6$	
d_η	f_a	$\sqrt{21}/7$	0	$-2/3$	0	
d_η	f_x	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$1/6$	
d_η	f_y	0	$-2/3$	0	0	
d_η	f_z	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$-1/6$	
d_η	f_ξ	$-\sqrt{21}/7$	0	$-1/6$	$-\sqrt{15}/6$	
d_η	f_η	0	0	0	0	
d_η	f_ζ	$\sqrt{21}/7$	0	$1/6$	$-\sqrt{15}/6$	
d_ζ	f_a	$\sqrt{21}/7$	0	$-2/3$	0	
d_ζ	f_x	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$-1/6$	
d_ζ	f_y	$-3\sqrt{35}/35$	0	$-\sqrt{15}/30$	$1/6$	
d_ζ	f_z	0	$-2/3$	0	0	
d_ζ	f_ξ	$\sqrt{21}/7$	0	$1/6$	$-\sqrt{15}/6$	
d_ζ	f_η	$-\sqrt{21}/7$	0	$-1/6$	$-\sqrt{15}/6$	
d_ζ	f_ζ	0	0	0	0	
d_θ	f_a	0	0	0	0	
d_θ	f_x	$-3\sqrt{105}/70$	0	$-2\sqrt{5}/15$	$\sqrt{3}/3$	
d_θ	f_y	$-3\sqrt{105}/70$	0	$-2\sqrt{5}/15$	$-\sqrt{3}/3$	
d_θ	f_z	$3\sqrt{105}/35$	0	$4\sqrt{5}/15$	0	
d_θ	f_ξ	$-3\sqrt{7}/14$	0	$\sqrt{3}/3$	0	
d_θ	f_η	$3\sqrt{7}/14$	0	$-\sqrt{3}/3$	0	
d_θ	f_ζ	0	0	0	0	
d_ϵ	f_a	0	0	0	0	
d_ϵ	f_x	$9\sqrt{35}/70$	0	$2\sqrt{15}/15$	$1/3$	
d_ϵ	f_y	$-9\sqrt{35}/70$	0	$-2\sqrt{15}/15$	$1/3$	
d_ϵ	f_z	0	0	0	$-2/3$	
d_ϵ	f_ξ	$-\sqrt{21}/14$	0	$1/3$	0	
d_ϵ	f_η	$-\sqrt{21}/14$	0	$1/3$	0	
d_ϵ	f_ζ	$\sqrt{21}/7$	0	$-2/3$	0	
ψ_i	ψ_j	$k=5(e_\theta)$	$k=5(e_\epsilon)$	$k=5(t_1^a)$	$k=5(t_1^b)$	$k=5(t_2)$
d_ξ	f_a	0	0	$5\sqrt{77}/231$	$-\sqrt{55}/11$	0
d_ξ	f_x	$5\sqrt{33}/66$	$5\sqrt{11}/66$	0	0	0
d_ξ	f_y	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$5\sqrt{11}/33$
d_ξ	f_z	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$-5\sqrt{11}/33$
d_ξ	f_ξ	$-\sqrt{55}/22$	$\sqrt{165}/22$	0	0	0
d_ξ	f_η	0	0	$-25\sqrt{77}/462$	$\sqrt{55}/22$	$-\sqrt{165}/33$
d_ξ	f_ζ	0	0	$25\sqrt{77}/462$	$-\sqrt{55}/22$	$-\sqrt{165}/33$
d_η	f_a	0	0	$5\sqrt{77}/231$	$-\sqrt{55}/11$	0
d_η	f_x	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$-5\sqrt{11}/33$
d_η	f_y	$-5\sqrt{33}/66$	$5\sqrt{11}/66$	0	0	0
d_η	f_z	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$5\sqrt{11}/33$
d_η	f_ξ	0	0	$25\sqrt{77}/462$	$-\sqrt{55}/22$	$-\sqrt{165}/33$

Table 2. (Continued)

ψ_i	ψ_j	$k = 5(\mathrm{e}_\theta)$	$k = 5(\mathrm{e}_\epsilon)$	$k = 5(t_1^a)$	$k = 5(t_1^b)$	$k = 5(t_2)$
d_η	f_η	$-\sqrt{55}/22$	$-\sqrt{165}/22$	0	0	0
d_η	f_ζ	0	0	$-25\sqrt{77}/462$	$\sqrt{55}/22$	$-\sqrt{165}/33$
d_ζ	f_a	0	0	$5\sqrt{77}/231$	$-\sqrt{55}/11$	0
d_ζ	f_x	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$5\sqrt{11}/33$
d_ζ	f_y	0	0	$5\sqrt{1155}/462$	$5\sqrt{33}/66$	$-5\sqrt{11}/33$
d_ζ	f_z	0	$-5\sqrt{11}/33$	0	0	0
d_ζ	f_ξ	0	0	$-25\sqrt{77}/462$	$\sqrt{55}/22$	$-\sqrt{165}/33$
d_ζ	f_η	0	0	$25\sqrt{77}/462$	$-\sqrt{55}/22$	$-\sqrt{165}/33$
d_ζ	f_ζ	$\sqrt{55}/11$	0	0	0	0
d_θ	f_a	0	$-\sqrt{55}/11$	0	0	0
d_θ	f_x	0	0	$-5\sqrt{385}/231$	0	$-5\sqrt{33}/66$
d_θ	f_y	0	0	$-5\sqrt{385}/231$	0	$5\sqrt{33}/66$
d_θ	f_z	0	0	$10\sqrt{385}/231$	0	0
d_θ	f_ξ	0	0	$-5\sqrt{231}/462$	$-\sqrt{165}/22$	$-\sqrt{55}/22$
d_θ	f_η	0	0	$5\sqrt{231}/462$	$\sqrt{165}/22$	$-\sqrt{55}/22$
d_θ	f_ζ	0	0	0	0	$\sqrt{55}/11$
d_ϵ	f_a	$\sqrt{55}/11$	0	0	0	0
d_ϵ	f_x	0	0	$5\sqrt{1155}/231$	0	$-5\sqrt{11}/66$
d_ϵ	f_y	0	0	$-5\sqrt{1155}/231$	0	$-5\sqrt{11}/66$
d_ϵ	f_z	0	0	0	0	$5\sqrt{11}/33$
d_ϵ	f_ξ	0	0	$-5\sqrt{77}/462$	$-\sqrt{55}/22$	$\sqrt{165}/22$
d_ϵ	f_η	0	0	$-5\sqrt{77}/462$	$-\sqrt{55}/22$	$-\sqrt{165}/22$
d_ϵ	f_ζ	0	0	$5\sqrt{77}/231$	$\sqrt{55}/11$	0

cubic symmetry. For example, a crystal field of rhombic symmetry can be described as one in which a cube is stretched along the symmetry axis (z) followed by a decrease in the area of the top face at $+z$ and an increase in the area of the bottom face at $-z$. The normal mode displacements are illustrated by Sturge for both octahedral and tetrahedral configurations [8], the latter being of interest in our example. The first distortion involving the stretching of the cube is a normal mode of e_θ symmetry. This can be seen from [8] or by examining the kubic harmonic $k = 2(\mathrm{e}_\theta)$ in table 1. The second distortion is a normal mode of $t_{2\zeta}$ symmetry. Hence, the crystal-field Hamiltonian can be written as

$$\mathcal{H} = V_{\mathrm{cub}}\mathcal{O}_{\mathrm{cub}} + V_{\mathrm{e}_\theta}\mathcal{O}_{\mathrm{e}_\theta} + V_{t_{2\zeta}}\mathcal{O}_{t_{2\zeta}} \tag{8}$$

where the V_i give the strengths of the different symmetry interactions and the $\mathcal{O}_i$ are the operators that take the form of the kubic harmonics ($\mathcal{O}_{\mathrm{cub}} \equiv k = 0(a_1)$). The relative matrix elements of these operators taken between atomic functions belonging to the same irreducible representation can be obtained from our table 2. The crystal-field interaction of equation (8) taken within d electrons is then

$$\mathcal{H} = \begin{pmatrix} -4Dq + V_{\mathrm{e}_\theta}^{t_2} & V_{t_{2\zeta}}^{t_2} & 0 & 0 & 0 \\ V_{t_{2\zeta}}^{t_2} & -4Dq + V_{\mathrm{e}_\theta}^{t_2} & 0 & 0 & 0 \\ 0 & 0 & -4Dq - 2V_{\mathrm{e}_\theta}^{t_2} & V_{t_{2\zeta}}^{t_2-\mathrm{e}} & 0 \\ 0 & 0 & V_{t_{2\zeta}}^{t_2-\mathrm{e}} & 6Dq + V_{\mathrm{e}_\theta}^{\mathrm{e}} & 0 \\ 0 & 0 & 0 & 0 & 6Dq - V_{\mathrm{e}_\theta}^{\mathrm{e}} \end{pmatrix} \tag{9}$$

where we have replaced the cubic-field coupling-strength parameter with the standard $10Dq$ used to define the cubic-field splitting between the e and t_2 d states. We note that this

Hamiltonian was written without ever having to expand the potential, that is expand $1/r_{ij}$, in rigorous mathematical fashion. This feature is particularly appealing when dealing with very low symmetry crystal fields. This clearly demonstrates the power and beauty of employing operators transforming as the kubic harmonics in the expansion of the crystal-field interaction.

As a final example, table 2 can be used to determine the expansion of the product of two kubic harmonics. The product of two kubic harmonics can be written as a linear combination of kubic harmonics. We find that

$$\mathrm{KH}_{lm}(x, y, z)\mathrm{KH}_{l'm'}(x, y, z) = \sum_{k=|l-l'|}^{l+l'} \sum_{q} c_{kq}(lm, l'm')\mathrm{KH}_{kq}(x, y, z). \quad (10)$$

That the expansion coefficients are simply the $c_{kq}(lm, l'm')$ from table 2 can be demonstrated in the usual fashion from the orthogonality of the kubic harmonics.

3. Conclusion

These tables enable those doing crystal-field-type calculations to work entirely within the kubic harmonic basis set for the electronic states. The use of this basis set has already been shown to facilitate the determination and interpretation of the crystal field at an impurity site, particularly sites of low symmetry. Up to now, however, one had to switch between electronic basis sets as the electron–electron interaction was calculated using the spherical harmonic basis set and the crystal field was calculated using the kubic harmonic basis set. We hope and expect that these tables will aid those performing future crystal-field-type calculations.

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