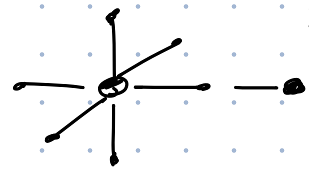
9. Crystallography symmetry

9.4. Splitting of atomic orbitals

Ref. Dresselhaus. Chap 5
Ballhausen. intro. to Ligand field theory Chap 4
Cowan. Theory of atomic structure and spectra

Consider an ion inside a crystal

SrTiO$_3$



$$H = H_f + V_{crystal}$$

free ion

① $$H_f = \sum_i \Big(\underbrace{\frac{p_i^2}{2m}}_{\text{kinetic}} - \underbrace{\frac{Z^* e^2}{r_i}}_{\text{e-ion Coulomb}} + \underbrace{\sum_j \frac{e^2}{r_{ij}}}_{\text{e-e}} + \underbrace{\xi_i \vec{l}_i \cdot \vec{s}_i}_{\text{spin-orbit}} \Big)$$

(ignore hyperfine etc.)

with spherical symmetry. We know the solution.

② $V_{crystal}$: external potential due to other ions in the crystal (Madelung potential for ionic systems.) "Crystal field".

a. $V_{crystal} < \xi \vec{l} \cdot \vec{s}$ rare-earths

b. $\xi \vec{l} \cdot \vec{s} < V$ transition metal compounds (Cu. Ni. etc.) magnetism. superconductivity

We focus on the second case. ignore SOC.

In this case. the symmetry-adapted basis functions are a better starting point than the atomic orbitals in spherical harmonics.

9.4.1. splitting of the V^ℓ rep.

For symmetry analysis. we can ignore the radial part of the basis functions. and consider Spherical harmonics $Y_{\ell m}(\theta, \phi)$

$$Y_{\ell m} = \left[\frac{2\ell+1}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{\frac{1}{2}} P_\ell^m(\cos\theta) e^{im\phi}$$

$$\left(\int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \, Y_{\ell m} \overline{Y_{\ell' m'}} = \delta_{\ell\ell'} \delta_{mm'} \right)$$

each ℓ labels an irrep

$$\hat{O}_R \cdot Y_{\ell m} = \sum D^\ell(R)_{m'm} Y_{\ell m'} \qquad \text{Wigner D-matrix}$$

① rotation around $\hat{z}$ by α then

$$\hat{O}_R Y_{\ell m}(\theta, \phi) = Y_{\ell m}(R^{-1}(\theta, \phi)) = e^{-im\alpha} Y_{\ell m}(\theta, \phi)$$

(we've seen it before)

$$\chi^\ell(\alpha) = \sum_m e^{-im\alpha} \underset{z = e^{-i\alpha/2}}{=} \frac{z^{2\ell+1} - z^{-2\ell-1}}{z - z^{-1}} = \frac{\sin(\ell+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}$$

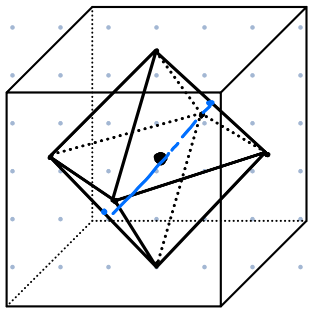
$$= U_\ell(\cos\frac{\alpha}{2})$$

chebyshev polynomial of the 2nd kind

② inversion $\hat{O}_i \cdot Y_{lm}(\theta, \phi) = Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi)$

$O_h = m3m$

$4/m\,\bar{3}\,2/m$



$C_3^{\pm}$ 3 body diagonals $\times \pm = 6$

C_2 connecting edge midpoints $\times 6$

$C_4(z)$ $3 \times C_4^{\pm} = 6$

$C_2(z)$ 3

$24 \times \{e, i\} = 48$

Now consider O_h with the character table below

$C_2(z)$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	-
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1	-	-	-
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_{1g}	+3	0	-1	+1	-1	+3	+1	0	-1	-1	(R_x, R_y, R_z)	-	-
T_{2g}	+3	0	+1	-1	-1	+3	-1	0	-1	+1	-	(xz, yz, xy)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
E_u	+2	-1	0	0	+2	-2	0	+1	-2	0	-	-	-
T_{1u}	+3	0	-1	+1	-1	-3	-1	0	+1	+1	(x, y, z)	-	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$

$\left(\frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha} \right)$

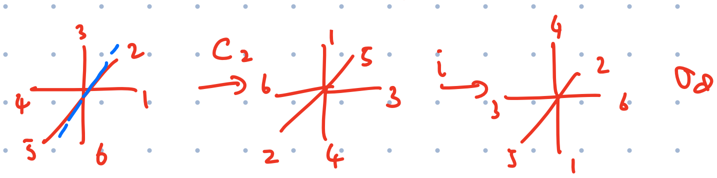
dim $(2l+1)$ $\quad \frac{2}{3}\pi \quad \pi \quad \frac{\pi}{2} \quad \pi$

$\chi(E) \quad \chi(C_3) \quad \chi(C_2) \quad \chi(C_4) \quad \chi(C_2)$

$i \quad iC_3 = S_6 \quad iC_2(xy) = \sigma_d \quad iC_4 = S_4 \quad iC_2(z) = \sigma_h$

① $iC_n = \sigma C_2 C_n = \sigma C_{2n}^{n+2} = S_{2n}^{n+2}$ odd: $iC_n = \sigma C_2 C_n = \sigma C_n^{\frac{n}{2}+1} = S_n^{\frac{n}{2}+1}$

②



	$\dim(2l+1)$ $\chi(E)$ i	$\frac{2}{3}\pi$ $\chi(C_3)$ S_6	π $\chi(C_2)$ σ_d	$\frac{\pi}{2}$ $\chi(C_4)$ S_4	π $\chi(C_2)$ σ_h	
① s-orbital $l=0$	1	1	1	1	1	$s \to A_{1g}$
	1	1	1	1	1	
② $p/l=1$	3	0	−1	1	−1	$p \to T_{1u}$
	−3	0	1	−1	1	
③ $d/l=2$	5	−1	1	−1	1	$d \to E_g + T_{2g}$
④ $f/l=3$	7	1	−1	−1	−1	$f \to A_{2u} + T_{1u} + T_{2u}$

$$\begin{cases} E_g:\ x^2-y^2,\ 3z^2-r^2 \\ T_{2g}:\ xy,\ yz,\ xz \end{cases}$$

9.4.2 Single d-electron in Octahedral field.

$l=2.\quad Y_l^m = \sqrt{\cancel{\frac{5}{4\pi}}\frac{(2-m)!}{(2+m)!}}\, P_l^m(\cos\theta)e^{im\varphi}$

ignore

$P_2^2(z) = 3(1-z^2) \qquad\qquad P_2^{-m}(z) = (-1)^m \frac{(2-m)!}{(2+m)!} P_2^m$

$P_2^1(z) = -3z(1-z^2)^{1/2}$

$P_2^0(z) = \frac{1}{2}(3z^2-1)$

write in x.y.z.

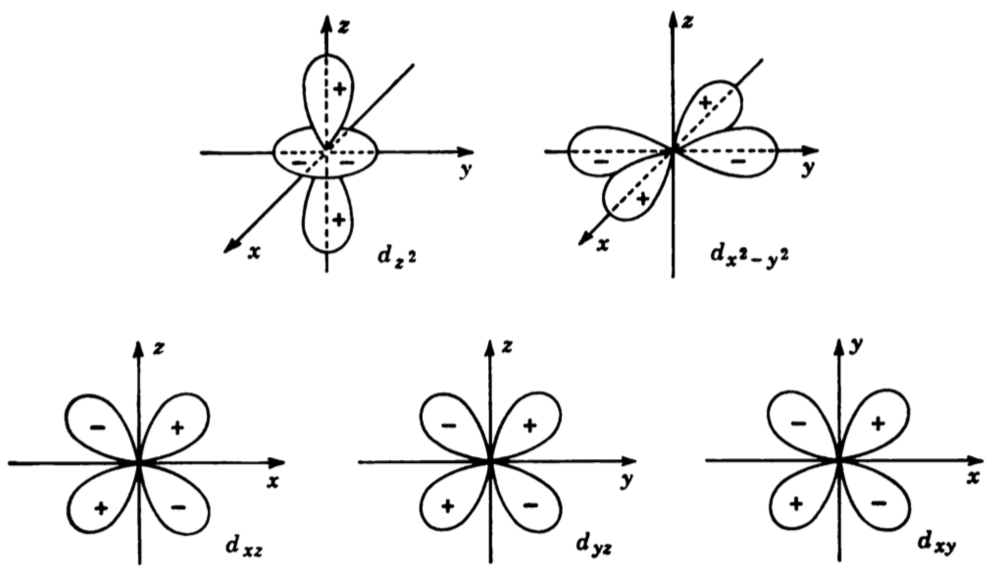
$$\begin{cases} x = \sin\theta\cos\varphi \\ y = \sin\theta\sin\varphi \\ z = \cos\theta \end{cases}$$

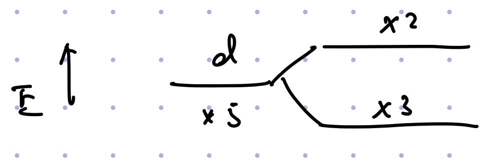
$$\begin{cases} d_{\pm 2} = Y_2^{\pm 2} = \sqrt{\frac{3}{8}}(x \pm iy)^2 \\ d_{\pm 1} = Y_2^{\pm 1} = \mp\sqrt{\frac{3}{2}}(x \pm iy)z \\ d_0 = Y_2^0 = \frac{1}{2}(3z^2-1) \end{cases}$$

$$\cos 2\phi$$

$$E_g: \begin{cases} x^2 - y^2 = \frac{1}{\sqrt{2}}(d_{+2} + d_{-2}) & \sim \sin^2\theta\,(\cos^2\phi - \sin^2\phi) \\ z^2 \to 3z^2 - 1 = d_0 & \sim \cos\theta \end{cases}$$

$$t_{2g} \begin{cases} xy & \frac{1}{\sqrt{2}i}(d_{+2} - d_{-2}) \sim \sin^2\theta\,(\sin\phi\cos\phi) \\ xz & -\frac{1}{\sqrt{2}}(d_{+1} - d_{-1}) \\ yz & -\frac{1}{\sqrt{2}i}(d_{+1} + d_{-1}) \end{cases}$$





e_g $E = 6Dq$

t_{2g} $E = -4Dq$

historically $10Dq$ splitting

the sign and amplitude determined by the physical details. $E_{eg} > E_{t_{2g}}$ because of charge distribution

Formally, we can expand $V_{crystal}$ onto spherical harmonics

$$V_c = \sum_i \sum_{\ell m} Y_\ell^m(\hat{r}_i) R_{n\ell}(r_i)$$

$$= \underset{\ell=0 \text{ part}}{V_R} + \underset{\text{octahedral part.}}{V_0}$$

It should has <u>all symmetries</u> of H. transform as $\overline{A_{1g}}$.
$(V_c = \sum_\mu \lambda^\mu \mathbb{1}_{\mu r})$

The potential for a d-electron:

$$\langle \ell_1 m_1 | V_c | \ell_2 m_2 \rangle \sim \begin{pmatrix} 2 & \ell & 2 \\ m_1 & m & -m_2 \end{pmatrix} \qquad \ell \le 4$$

We can further ignore odd orders because d electrons are even. $(\ell = 2)$

Remaining terms are Y_2^m and Y_4^m.

Y_2^m : $E_g \oplus T_{2g}$. no A_{1g} component

Y_4^m : $\underline{\underline{A_{1g}}} \oplus E_g \oplus T_{1g} \oplus T_{2g}$

$\Rightarrow$ find that $V_0 = Y_4^0 + \sqrt{\frac{5}{14}}\,(Y_4^4 + Y_4^{-4})$

(axis dependent.)

Check: $\hat{C}_4 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ -x \\ z \end{pmatrix}$

$$\hat{C}_4 Y_4^{\pm 4} = Y_4^{\pm 4} \qquad Y_4^{\pm 4} \propto \sin^4\theta\, e^{\pm i 4\phi}$$

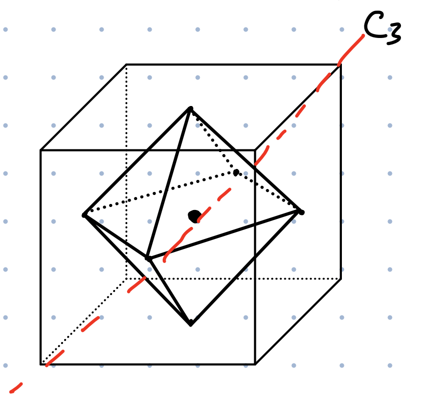
One can then write out the matrix elements of V_o in d_m. ignore prefactors $\langle Y_2^m | Y_4^0 + \sqrt{\frac{5}{14}}(Y_4^4 + Y_4^{-4}) | Y_2^{m'} \rangle$

$$\frac{1}{21}\begin{pmatrix} 1 & & & & 5 \\ & -4 & & & \\ & & 6 & & \\ & & & -4 & \\ 5 & & & & 1 \end{pmatrix}$$

$E(E_g) = \frac{6}{21} = 6Dq$

$E(T_{2g}) = -\frac{4}{21} = -4Dq$

Note that the form of E_g/T_{2g} orbitals depend on the quantization axis. If choosing C_3 as the quantization axis. then



$$E_g = \begin{cases} \sqrt{\frac{1}{3}}\, d_2 + \sqrt{\frac{2}{3}}\, d_{-1} \\ \sqrt{\frac{1}{3}}\, d_{-2} - \sqrt{\frac{2}{3}}\, d_1 \end{cases}$$

$$T_{2g} = \begin{cases} d_0 \\ \sqrt{2/3}\, d_2 - \sqrt{1/3}\, d_1 \\ \sqrt{2/3}\, d_{-2} + \sqrt{1/3}\, d_1 \end{cases}$$

$$V_c = Y_4^0 + \sqrt{\frac{10}{7}}\,(Y_4^3 - Y_4^{-3})$$

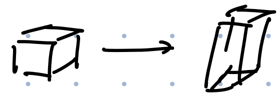
$$(V_c)_{mm'} = \frac{1}{21}\begin{pmatrix} 1 & & & \frac{5}{21}\sqrt{2} & \\ & -4 & & & -\frac{5}{21}\sqrt{2} \\ & & 6 & & \\ \frac{5}{21}\sqrt{2} & & & -4 & \\ & -\frac{5\sqrt{2}}{21} & & & 1 \end{pmatrix}$$

$E(E_g) = -\frac{3}{7}$

$E(T_{2g}) = \frac{2}{7}$

The sign of $10Dq$ is reversed.

Now consider $O_h \to D_{4h}$



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i
A_{1g}	+1	+1	+1	+1	+1	
A_{2g}	+1	+1	-1	-1	+1	
E_g	+2	-1	0	0	+2	
T_{1g}	+3	0	-1	+1	-1	
T_{2g}	+3	0	+1	-1	-1	

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-

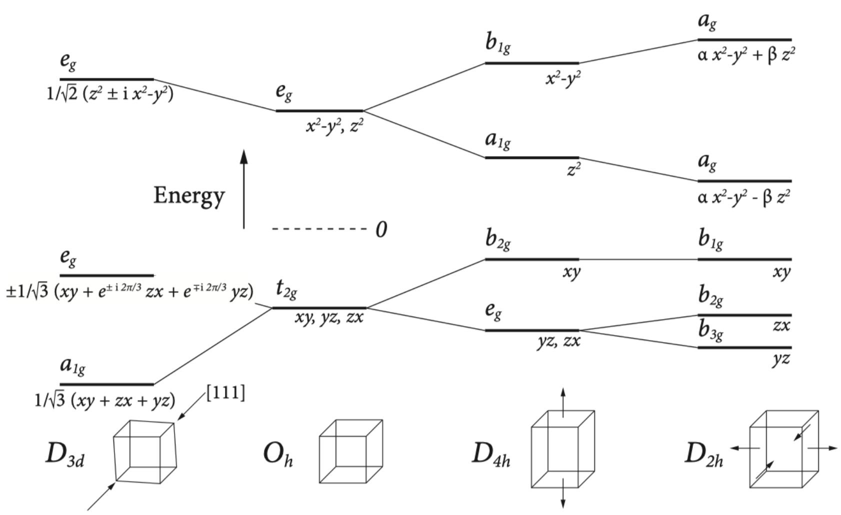
O_h $\tilde{E}_g$ 2 0 2 2 0

$\tilde{T}_{2g}$ 3 1 -1 -1 -1

O_h D_{4h}

$E_g \to A_{1g} + B_{1g}$ $T_{2g} \to B_{2g} + E_g$

z^2 x^2-y^2 xy xz, yz



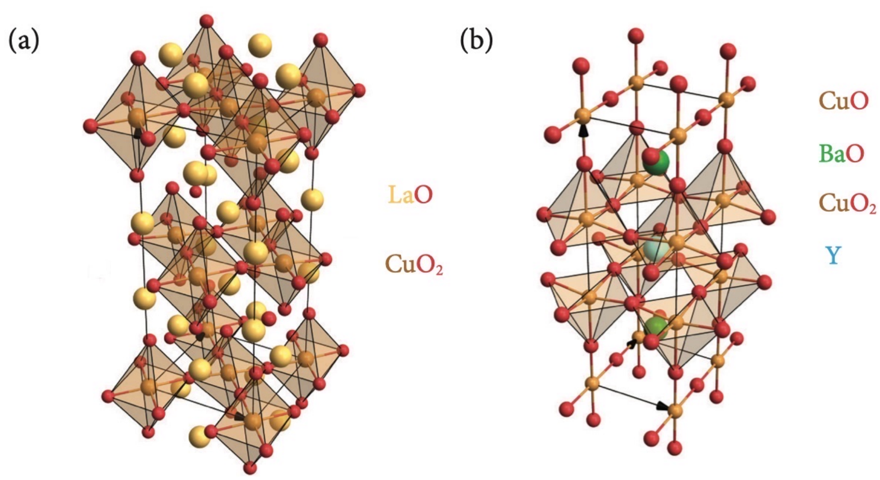


Figure 2.8 | Structures of (a) La_2CuO_4 and (b) $YBa_2Cu_3O_7$.

Cu^{2+}: $3d^9$

b_{2g} ↑ x^2-y^2

a_{1g} ↑↓ $3z^2-r$

b_{2g} ↑↓ xy

e_g ↑↓↑↓ xz/yz

Character table for point group O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 =(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	-
A_{2g}	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1	-	-	-
E_g	+2	-1	0	0	+2	+2	0	-1	+2	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
T_{1g}	+3	0	-1	+1	-1	+3	+1	0	-1	-1	(R_x, R_y, R_z)	-	-
T_{2g}	+3	0	+1	-1	-1	+3	-1	0	-1	+1	-	(xz, yz, xy)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
E_u	+2	-1	0	0	+2	-2	0	+1	-2	0	-	-	-
T_{1u}	+3	0	-1	+1	-1	-3	-1	0	+1	+1	(x, y, z)	-	(x^3, y^3, z^3) $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$

http://symmetry.jacobs-university.de/cgi-bin/group.cgi?group=904&option=4

Character table for point group D_{4h}

(x axis coincident with C'_2 axis)

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-	$z^3, z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)

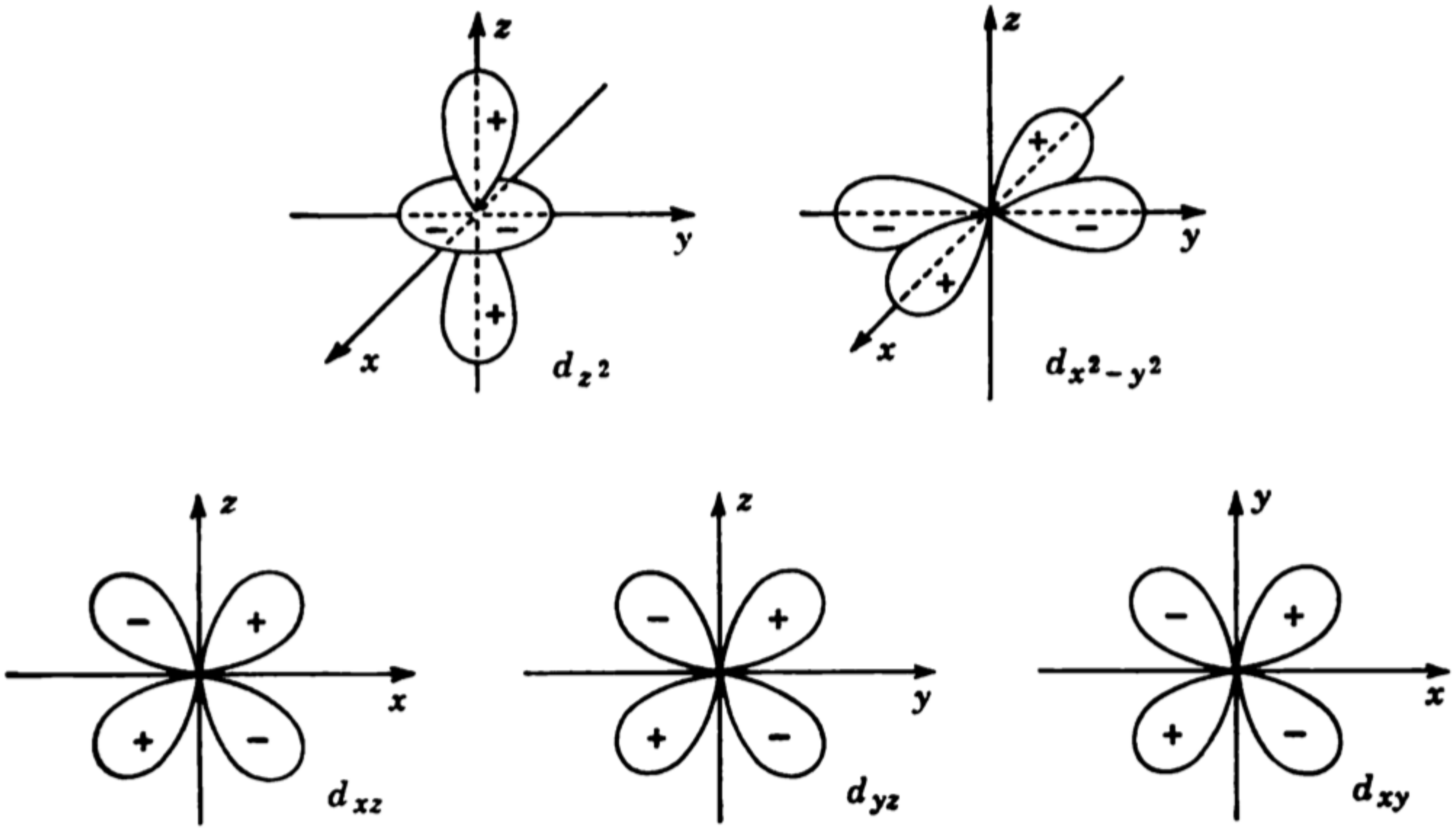
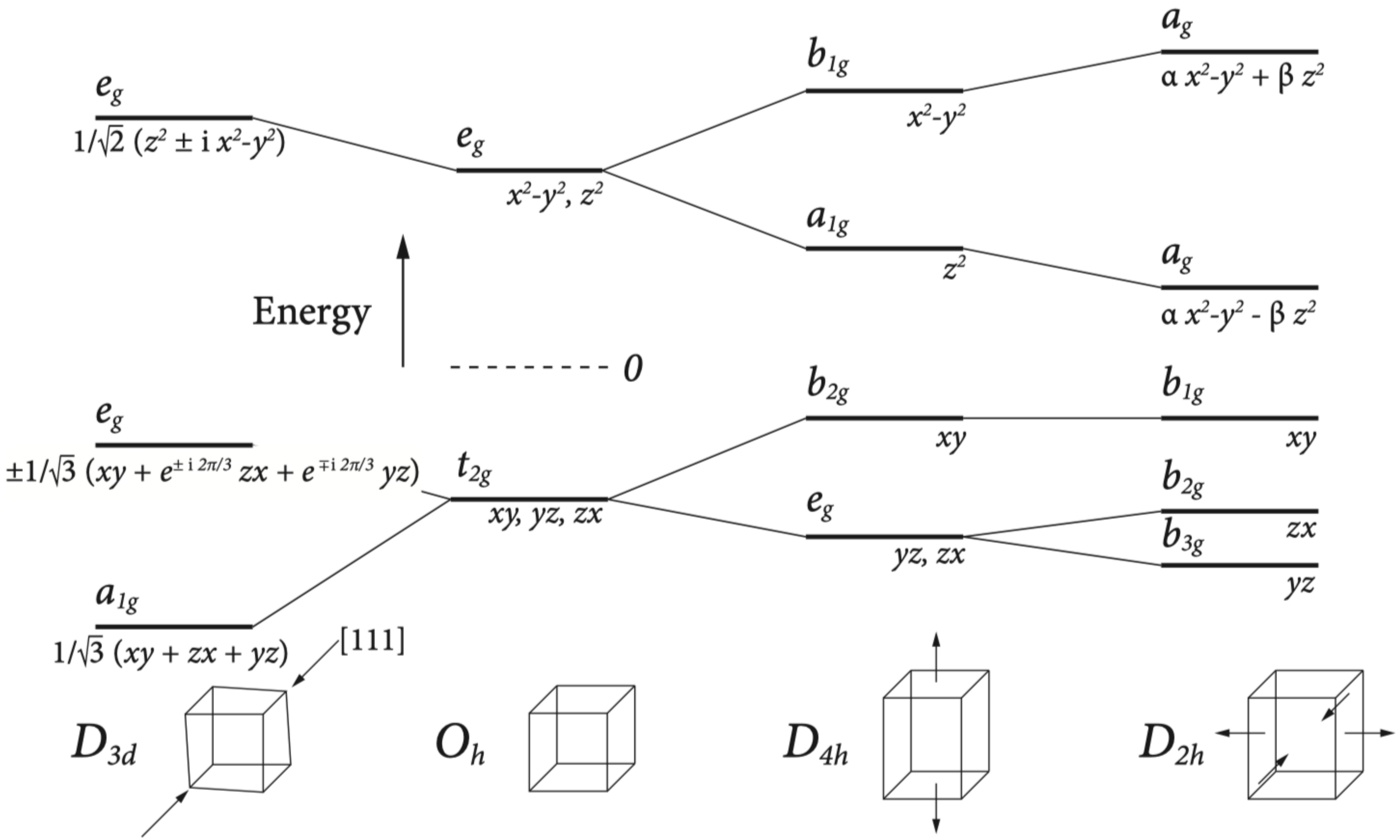
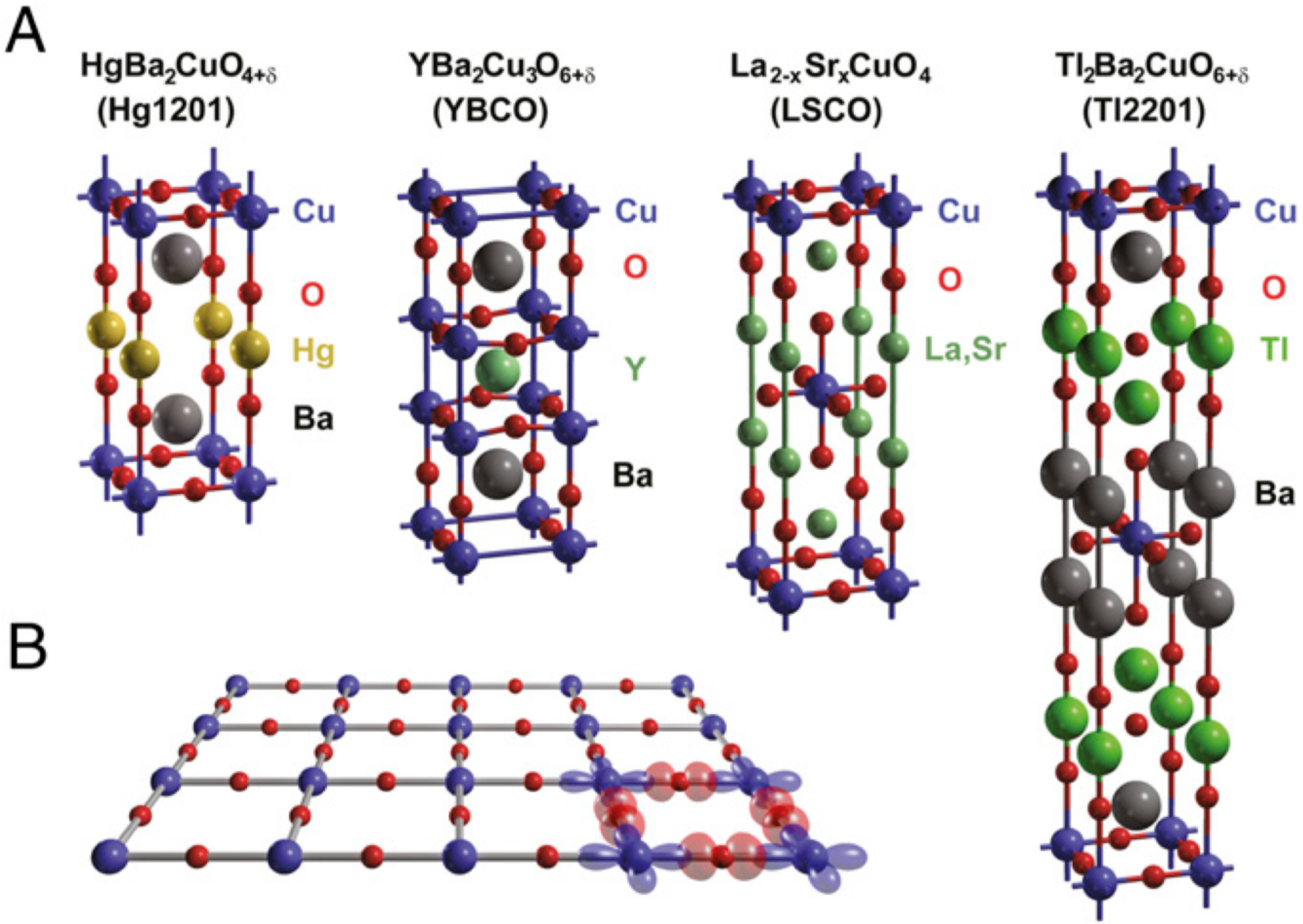


FIG. 4-1. e_g and t_{2g} electronic densities.



e_g
1/√2 (z² ± i x²-y²)
e_g
x²-y², z²
b_1g
x²-y²
a_1g
z²
a_g
α x²-y² + β z²
a_g
α x²-y² - β z²
Energy
0
e_g
±1/√3 (xy + e^{±i 2π/3} zx + e^{∓i 2π/3} yz)
t_2g
xy, yz, zx
b_2g
xy
e_g
yz, zx
b_1g
xy
b_2g
zx
b_3g
yz
a_1g
1/√3 (xy + zx + yz)
[111]
D_3d
O_h
D_4h
D_2h



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