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Chapter 6

Consequences of Crystallographic Symmetry

6.1 Atomic Physics and the Periodic Table

First, some atomic physics[1]. The eigenspectrum of single electron hydrogenic atoms is specified by quantum numbers $n \in \{1, 2, \ldots\}$, $l \in \{0, 1, \ldots, n-1\}$, $m_l \in \{-l, \ldots, +l\}$, and $m_s = \pm\frac{1}{2}$. The bound state energy eigenvalues $E_{nl} = -e^2/2na_{\text{B}}$, where $a_{\text{B}} = \hbar^2/me^2 = 0.529\,\text{Å}$ is the Bohr radius, depend only on the principal quantum number n. Accounting for electron-electron interactions using the Hartree-Fock method[2], the essential physics of *screening* is introduced, a result of which is that states of different l for a given n are no longer degenerate. Smaller l means lower energy since those states are localized closer to the nucleus, where the potential is less screened. Thus, for a given n, the smaller l states fill up first. For a given n and l, there are $(2s+1) \times (2l+1) = 4l+2$ states, labeled by m_l and m_s. This group of orbitals is called a *shell*.

6.1.1 Aufbau principle

Based on the HF energy levels, the order in which the electron shells are filled throughout the periodic table is roughly given by that in Tab. 6.1. This is known as the *Aufbau principle* from the German *Aufbau* = "building up". The order in which the orbitals are filled follows the *diagonal rule*, which says that orbitaPoisson bra ls with lower values of $n+l$ are filled before those with higher values, and that in the case of equal $n+l$ values, the orbital with the lower n is filled first. There are hiccups here and there. For example, in filling the 3d shell of the transition metal series (row four of the PT) , ^{21}Sc, ^{22}Ti, and ^{23}V, are configured as $[\text{Ar}]\,4\text{s}^2\,3\text{d}^1$, $[\text{Ar}]\,4\text{s}^2\,3\text{d}^2$, and $[\text{Ar}]\,4\text{s}^2\,3\text{d}^3$, respectively, but chromium's (dominant) configuration is $[\text{Ar}]\,4\text{s}^1\,3\text{d}^5$. Similarly, copper is $[\text{Ar}]\,4\text{s}^1\,3\text{d}^{10}$ rather than the expected $[\text{Ar}]\,4\text{s}^2\,3\text{d}^9$. For

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[1] An excellent discussion is to be found in chapter 20 of G. Baym's *Lectures on Quantum Mechanics*.

[2] Hartree-Fock theory tends to overestimate ground state atomic energies by on the order of 1 eV per pair of electrons. The reason is that electron-electron correlations are not adequately represented in the Hartree-Fock many-body wavefunctions, which are single Slater determinants.

Figure 6.1: The *Aufbau* principle and the diagonal rule. Image credit: Wikipedia.

palladium, the diagonal rule predicts an electronic configuration [Kr] $5s^2\,4d^8$ whereas experiments say it is [Kr] $5s^0\,4d^{10}$ Go figure. Again, don't take this shell configuration stuff too seriously, because the atomic ground states are really linear combinations of different shell configurations, so we should really think of these various configurations as being the dominant ones among a more general linear combination of states. Row five pretty much repeats row four, with the filling of the 5s, 4d, and 5p shells. In row six, the lanthanide (4f) series interpolates between the 6s and 5d shells, as the 5f actinide series interpolates in row seven between 7s and 6d.

shell:	1s	2s	2p	3s	3p	4s	3d	4p	5s
termination:	^{2}He	^{4}Be	^{10}Ne	^{12}Mg	^{18}Ar	^{20}Ca	^{30}Zn	^{36}Kr	^{38}Sr
shell:	4d	5p	6s	4f	5d	6p	7s	5f/6d	
termination:	^{48}Cd	^{54}Xe	^{56}Ba	^{71}Lu	^{80}Hg	^{86}Rn	^{88}Ra	^{102}No	

Table 6.1: Rough order in which shells of the periodic table are filled.

6.1.2 Splitting of configurations: Hund's rules

The electronic configuration does not uniquely specify a ground state. Consider, for example, carbon, whose configuration is $1s^2\,2s^2\,2p^2$. The filled 1s and 2s shells are inert. However, there are $\binom{6}{2} = 15$ possible ways to put two electrons in the 2p shell. It is convenient to label these states by total L, S, and J quantum numbers, where $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is the total angular momentum. It is standard to abbreviate each such multiplet as a *term* $^{2S+1}L_J$, where $L =$ S, P, D, F, G, *etc.*. For carbon, the largest L value we can get is $L = 2$, which requires $S = 0$ and hence $J = L = 2$. This 5-fold degenerate multiplet is then abbreviated $^1\mathrm{D}_2$. But we can also add together two $l = 1$ states to get total angular momentum $L = 1$ as well. The corresponding spatial wavefunction is antisymmetric, hence $S = 1$ in order to achieve a symmetric spin wavefunction. Since $|L - S| \le J \le |L + S|$ we have $J = 0$, $J = 1$, or $J = 2$ corresponding to multiplets $^3\mathrm{P}_0$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_2$, with degeneracy 1, 3, and 5, respectively. The final state has $J = L = S = 0$: $^1\mathrm{S}_0$. The Hilbert space is then spanned by two $J = 0$ singlets, one $J = 1$ triplet, and two $J = 2$ quintuplets: $0 \oplus 0 \oplus 1 \oplus 2 \oplus 2$. That makes 15 states. Which of these terms corresponds to the

3d transition metal series ([Ar] core)									
^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn
$4s^2\,3d^1$	$4s^2\,3d^2$	$4s^2\,3d^3$	$4s^1\,3d^5$	$4s^2\,3d^5$	$4s^2\,3d^6$	$4s^2\,3d^7$	$4s^2\,3d^8$	$4s^1\,3d^{10}$	$4s^2\,3d^{10}$

Table 6.2: Electronic configuration of 3d-series metals.

ground state?

The ordering of the multiplets is determined by the famous *Hund's rules*:

1. The LS multiplet with the *largest* S has the lowest energy.
2. If the largest value of S is associated with several multiplets, the multiplet with the *largest* L has the lowest energy.
3. If an incomplete shell is not more than half-filled, then the lowest energy state has $J = |L - S|$. If the shell is more than half-filled, then $J = L + S$.

Hund's rules are largely empirical, but are supported by detailed atomic quantum many-body calculations. Basically, rule #1 prefers large S because this makes the spin part of the wavefunction maximally symmetric, which means that the spatial part is maximally antisymmetric. Electrons, which repel each other, prefer to exist in a spatially antisymmetric state. As for rule #2, large L expands the electron cloud somewhat, which also keeps the electrons away from each other. For neutral carbon, the ground state has $S = 1$, $L = 1$, and $J = |L - S| = 0$, hence the ground state term is $^3\mathrm{P}_0$.

Let's practice Hund's rules on a couple of ions:

- P : The electronic configuration for elemental phosphorus is $[\mathrm{Ne}]\,3s^2\,3p^3$. The unfilled 3d shell has three electrons. First maximize S by polarizing all spins parallel (up, say), yielding $S = \frac{3}{2}$. Next maximize L consistent with Pauli exclusion, which says $L = -1 + 0 + 1 = 0$. Finally, since the shell is exactly half-filled, and not more, $J = |L - S| = \frac{3}{2}$, and the ground state term is $^4\mathrm{S}_{3/2}$.
- Mn^{4+} : The electronic configuration $[\mathrm{Ar}]\,4s^0\,3d^3$ has an unfilled 3d shell with three electrons. First maximize S by polarizing all spins parallel, yielding $S = \frac{3}{2}$. Next maximize L consistent with Pauli exclusion, which says $L = 2 + 1 + 0 = 3$. Finally, since the shell is less than half-filled, $J = |L - S| = \frac{3}{2}$. The ground state term is $^4\mathrm{F}_{3/2}$.
- Fe^{2+} : The electronic configuration $[\mathrm{Ar}]\,4s^0\,3d^6$ has an unfilled 3d shell with six electrons, or four holes. First maximize S by making the spins of the holes parallel, yielding $S = 2$. Next, maximize L consistent with Pauli exclusion, which says $L = 2 + 1 + 0 + (-1) = 2$ (adding L_z for the four holes). Finally, the shell is more than half-filled, which means $J = L + S = 4$. The ground state term is $^5\mathrm{D}_4$.
- Nd^{3+} : The electronic configuration $[\mathrm{Xe}]\,6s^0\,4f^3$ has an unfilled 4f shell with three electrons. First maximize S by making the electron spins parallel, yielding $S = \frac{3}{2}$. Next, maximize L consistent

n_p	0	1	2	3	4	5	6								
L	0	1	1	0	1	1	0								
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0								
J	0	$\frac{1}{2}$	0	$\frac{3}{2}$	2	$\frac{3}{2}$	0								
n_d	0	1	2	3	4	5	6	7	8	9	10				
L	0	2	3	3	2	0	2	3	3	2	0				
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	2	$\frac{3}{2}$	1	$\frac{1}{2}$	0				
J	0	$\frac{3}{2}$	2	$\frac{3}{2}$	0	$\frac{5}{2}$	4	$\frac{9}{2}$	4	$\frac{5}{2}$	0				
n_f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
L	0	3	5	6	6	5	3	0	3	5	6	6	5	3	0
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	3	$\frac{5}{2}$	2	$\frac{3}{2}$	1	$\frac{1}{2}$	0
J	0	$\frac{5}{2}$	4	$\frac{9}{2}$	4	$\frac{5}{2}$	0	$\frac{7}{2}$	6	$\frac{15}{2}$	8	$\frac{15}{2}$	6	$\frac{7}{2}$	0

Table 6.3: Hund's rules applied to p, d, and f shells.

with Pauli exclusion: $L = 3 + 2 + 1 = 6$. Finally, because the shell is less than half-filled, we have $J = |L - S| = \frac{9}{2}$. The ground state term is ${}^4\mathrm{I}_{9/2}$.

For high Z ions, spin-orbit effects are very strong, and one cannot treat the angular momentum and spin degrees of freedom of the individual electrons separately. Rather, the electrons are characterized by their total angular momentum j, and the LS (Russell-Saunders) coupling scheme which gives rise to Hund's rules crosses over to another scheme called jj coupling[3]. In practice, pure jj coupling is rare, and the electronic structure of high Z atoms and ions reflects some intermediate situation between pure LS and pure jj schemes.

6.2 Crystal Field Theory

The Hamiltonian of an isolated atom or ion has the full rotational symmetry of $\mathsf{O}(3)$. In a crystalline environment, any electrons in an unfilled outer shell experience a *crystal electric field* due to the charges of neighboring ions. This breaks $\mathsf{O}(3)$ down to a discrete site group $\mathcal{P}(\boldsymbol{r})$, resulting in a new multiplet structure classified by the IRREPs of $\mathcal{P}(\boldsymbol{r})$. The program is therefore to identify the representation of $\mathsf{SO}(3)$ (possibly with half-odd-integer angular momentum) and decompose it into the IRREPs of the

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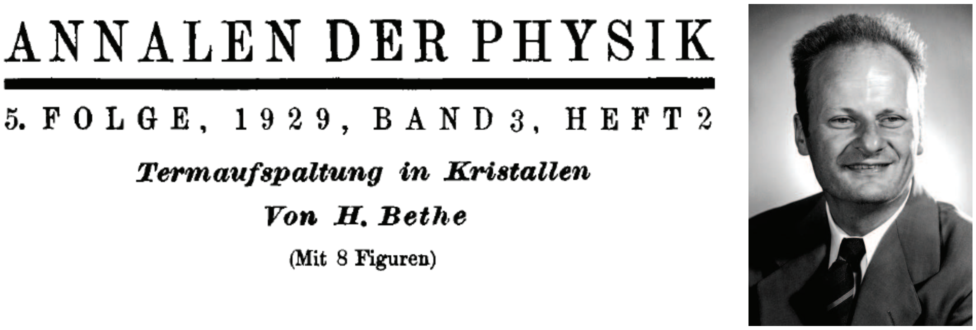
[3] See, *e.g.*, P. H. Heckmann and E. Träbert, *Introduction to the Spectroscopy of Atoms* (North-Holland, 1989).



ANNALEN DER PHYSIK

5. FOLGE, 1929, BAND 3, HEFT 2

Termaufspaltung in Kristallen

Von H. Bethe

(Mit 8 Figuren)

Figure 6.2: Title from Bethe's original article on term splitting in crystals, *Ann. der Physik* **395**, 133-208 (1929), and a photo of Bethe.

appropriate site group using the decomposition formula

$$n_\Gamma(\Psi) = \frac{1}{N_G} \sum_{\mathcal{C}} N_{\mathcal{C}}\, \chi^{\Gamma^*}(\mathcal{C})\, \chi^{\Psi}(\mathcal{C}) \quad . \tag{6.1}$$

If the crystal is symmorphic and the ion sits at a site of maximal symmetry, then the decomposition is with respect to the crystallographic point group $\mathcal{P}$. The foundations of this analysis were laid in 1929 by Hans Bethe in a seminal paper entitled *Termsaufspaltung in Kristallen* (”term splitting in crystals”).

6.2.1 Decomposing IRREPs of O(3)

Our first order of business is to obtain the characters of the various point group class representatives in the representations of SO(3), $\chi^J(\mathcal{C})$, and then to invoke Eqn. 6.1 to decompose the terms ${}^{2S+1}L_J$ into the point group IRREPs[4] The individual classes $\mathcal{C}$ will contain elements which are either rotations $C(\alpha)$ through an angle α about an axis, inversion I, reflections in a plane $\sigma = I\,C(\pi)$, or rotoreflections $S(\alpha) = I\,C(\alpha - \pi)$. We consider each of these in turn:

- *Identity* : The character of the identity is the dimension of the O(3) IRREP. Thus $\chi^J(E) = 2J + 1$.
- *Proper rotations* : Recall how the group character, being the trace of a representation matrix, is invariant under a similarity transformation, and upon rotating to a frame where the invariant axis is $\hat{\boldsymbol{z}}$, the trace of the rotation matrix $D(\alpha, \hat{\boldsymbol{z}}) = \exp(-i\alpha J^z)$ is

$$\chi^J(\alpha) = \frac{\sin\,(J + \frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha} \tag{6.2}$$

- *Inversion* : The inversion element I commutes with all other point group operations. Since $I^2 = 1$, the inversion eigenvalue is $\eta = \pm 1$. This is called the *parity*. For a single atomic orbital of angular momentum l, we have $\eta = (-1)^l$. But for the term ${}^{2S+1}L_J$, the parity is $\eta = \prod_i (-1)^{l_i}$, where l_i is

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[4] When the ion is located at a site which is not of maximal symmetry, $\mathcal{P}$ will refer to the appropriate site group.

the angular momentum of the i^{th} electron state in the electron configuration associated with each term. Thus, if there are n electrons in the angular momentum l shell, the parity is $\eta = (-1)^{nl}$ which is not necessarily the same as $(-1)^L$. For example, the ground state term of nitrogen is ${}^4\text{S}_{3/2}$, hence $L = 0$. But the corresponding electron configuration is $1\text{s}^2\,2\text{s}^2\,2\text{p}^3$, hence $\eta = -1$. The character of the inversion operator is $\chi^J(I) = (2J+1)\,\eta$.

- *Reflections* : Every reflection can be written as $\sigma = I\,C(\pi)$. Therefore since I commutes with $C(\pi)$, their eigenvalues multiply and we have $\chi^J(\sigma) = \eta\,\sin(J+\frac{1}{2})\pi$.

- *Rotoreflections* : Since $S(\alpha) = I\,C(\alpha-\pi)$, we have $\chi^J(\widetilde{\alpha}) = \chi^J(\alpha-\pi)\,\eta$, where $\widetilde{\alpha}$ denotes rotoreflection through angle α.

We will first consider the case where $J \in \mathbb{Z}$, so we do not need to invoke the double groups. Another possible setting is that we might be neglecting spin-orbit effects and considering individual atomic orbitals of angular momentum l, in which case the parity is $\eta = (-1)^l$. For point group proper rotations, we have from Eqn. 6.2,

$$\chi^J(\pi) = \begin{cases} +1 & \text{if } J = 2k \\ -1 & \text{if } J = 2k+1 \end{cases} \quad , \qquad \chi^J(2\pi/3) = \begin{cases} +1 & \text{if } J = 3k \\ 0 & \text{if } J = 3k+1 \\ -1 & \text{if } J = 3k+2 \end{cases} \tag{6.3}$$

and

$$\chi^J(\pi/2) = \begin{cases} +1 & \text{if } J = 4k \\ +1 & \text{if } J = 4k+1 \\ -1 & \text{if } J = 4k+2 \\ -1 & \text{if } J = 4k+3 \end{cases} \quad , \qquad \chi^J(\pi/3) = \begin{cases} +1 & \text{if } J = 6k \\ +2 & \text{if } J = 6k+1 \\ +1 & \text{if } J = 6k+2 \\ -1 & \text{if } J = 6k+3 \\ -2 & \text{if } J = 6k+4 \\ -1 & \text{if } J = 6k+5 \end{cases} \quad . \tag{6.4}$$

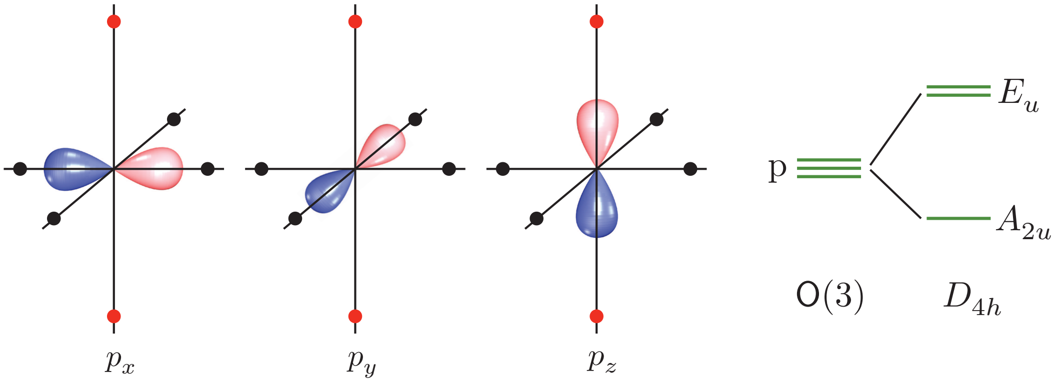

Figure 6.3: Atomic p orbital in a tetragonal environment with D_{4h} symmetry.

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	basis
A_1	1	1	1	1	1	x^2+y^2 or z^2
A_2	1	1	1	-1	-1	z or L_z
B_1	1	-1	1	1	-1	x^2-y^2
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	$\{x\,,\,y\}$ or $\{xz\,,\,yz\}$
1^- (p)	3	1	-1	-1	-1	$A_2 \oplus E$
2^+ (d)	5	-1	1	1	1	$A_1 \oplus B_1 \oplus B_2 \oplus E$

Table 6.4: Character table of D_4 and decomposition of atomic p- and d- levels in a D_4 environment. Note that $D_{4h} = D_4 \times C_i$.

6.2.2 Atomic levels in a tetragonal environment

Let's first consider a simple case of an atomic p-level placed in a tetragonal environment with D_4 symmetry, as depicted in Fig. 6.3. In free space, the p level is triply degenerate. Since D_4 is a proper point group, we only need the characters for the operations E, C_2, and C_4, which, according to the above computations, are

$$\chi^{l=1}(E) = 3 \quad , \quad \chi^{l=1}(C_2) = -1 \quad , \quad \chi^{l=1}(C_3) = 0 \quad , \quad \chi^{l=1}(C_4) = +1 \quad , \tag{6.5}$$

where we've included $\chi^{l=1}(C_3)$ as a bonus character. Using the representation decomposition formula of Eqn. 6.1, we then find $1^- = A_2 \oplus E$.

Suppose our environment has the full D_{4h} symmetry and not only D_4. Now $D_{4h} = D_4 \times C_i$, where $C_i = \{E, I\} \cong \mathbb{Z}_2$, and we know (see §2.4.6) that for an arbitrary group G, each conjugacy class $\mathcal{C}$ in G has a double $I\mathcal{C}$ in $G \times \mathbb{Z}_2$, and furthermore that each IRREP Γ of G spawns two IRREPs $\Gamma^{\pm}$ (also called Γ_g and Γ_u) for $G \times \mathbb{Z}_2$, with $\chi^{\Gamma^{\pm}}(\mathcal{C}) = \chi^{\Gamma}(\mathcal{C})$ and $\chi^{\Gamma^{\pm}}(I\,\mathcal{C}) = \pm\chi^{\Gamma}(\mathcal{C})$. Since p-states have parity $\eta = (-1)^l = -1$, we immediately know that in a D_{4h} environment, $1^- = A_{2u} \oplus E_u$.

What happens if we place an atomic d level in a tetragonal environment with D_{4h} symmetry? In this case we have

$$\chi^{l=2}(E) = 5 \quad , \quad \chi^{l=2}(C_2) = +1 \quad , \quad \chi^{l=2}(C_3) = -1 \quad , \quad \chi^{l=2}(C_4) = -1 \quad . \tag{6.6}$$

Accordingly we find $2^+ = A_1 \oplus B_1 \oplus B_2 \oplus E$ in D_4, and of course $2^+ = A_{1g} \oplus B_{1g} \oplus B_{1g} \oplus E_g$ in D_{4h}. Note that the labels u and g apply only when the site group symmetry includes inversion. Accordingly, in Tab. 6.6, the IRREPs for the two proper point groups T_d and D_3 do not include the g or u label.

6.2.3 Point charge model

We can understand the splitting of atomic levels in terms of the local crystal field potential due to the neighboring ions, which breaks the continuous O(3) atomic symmetry. Consider an electron at position

O	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$	basis
$\Gamma = A_1$	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	$L_x\,L_y\,L_z$ (sixth order in $\boldsymbol{r}$)
E	2	-1	2	0	0	$\big\{\sqrt{3}\,(x^2-y^2)\,,\,3z^2-r^2\big\}$
T_1	3	0	-1	-1	1	$\big\{x\,,\,y\,,\,z\big\}$
T_2	3	0	-1	1	-1	$\big\{yz\,,\,zx\,,\,xy\big\}$
$J^\eta = 0^\pm$	1	1	1	1	1	A_1
$1^\pm$	3	0	-1	-1	1	T_1
$2^\pm$	5	-1	1	1	-1	$E \oplus T_2$
$3^\pm$	7	1	-1	-1	-1	$A_2 \oplus T_1 \oplus T_2$
$4^\pm$	9	0	1	1	1	$A_1 \oplus E \oplus T_1 \oplus T_2$
$5^\pm$	11	-1	-1	-1	1	$E \oplus 2T_1 \oplus T_2$

Table 6.5: Character table of O and decomposition of $\mathsf{O}(3)$ IRREPs in terms of O IRREPs.

$\boldsymbol{r}$ in the vicinity of the origin, and the electrostatic potential arising from a fixed ion at position $\boldsymbol{\Delta}$ (not necessarily a direct lattice vector). The Coulomb potential is proportional to

$$\frac{1}{|\boldsymbol{\Delta}-\boldsymbol{r}|} = \frac{1}{\Delta}\big(1-2\hat{\boldsymbol{\Delta}}\cdot\boldsymbol{u}+u^2\big)^{-1/2} \quad , \tag{6.7}$$

where $\boldsymbol{u} \equiv \boldsymbol{r}/\Delta$ and $\hat{\boldsymbol{\Delta}} \equiv \boldsymbol{\Delta}/\Delta$. Define $\varepsilon \equiv 2\hat{\boldsymbol{\Delta}}\cdot\boldsymbol{u} - u^2$. Then from Taylor's theorem,

$$(1-\varepsilon)^{-1/2} = 1 + \tfrac{1}{2}\,\varepsilon + \tfrac{3}{8}\,\varepsilon^2 + \tfrac{5}{16}\,\varepsilon^3 + \tfrac{35}{128}\,\varepsilon^4 + \ldots \quad . \tag{6.8}$$

We then have, keeping terms up to order u^4, and restoring the dimensionful variables,

$$\begin{aligned}\frac{1}{|\boldsymbol{\Delta}-\boldsymbol{r}|} = \frac{1}{\Delta} + \frac{\boldsymbol{\Delta}\cdot\boldsymbol{r}}{\Delta^3} + \frac{3\,(\boldsymbol{\Delta}\cdot\boldsymbol{r})^2 - \Delta^2\,r^2}{2\Delta^5} + \frac{5(\boldsymbol{\Delta}\cdot\boldsymbol{r})^3 - 3\Delta^2\,(\boldsymbol{\Delta}\cdot\boldsymbol{r})\,r^2}{2\Delta^7}\\ + \frac{35(\boldsymbol{\Delta}\cdot\boldsymbol{r})^4 - 30\Delta^2\,(\boldsymbol{\Delta}\cdot\boldsymbol{r})^2\,r^2 + 3\Delta^4\,r^4}{8\Delta^9} + \ldots \quad .\end{aligned} \tag{6.9}$$

The local potential is given by

$$V(\boldsymbol{r}) = -\sum_{\boldsymbol{\Delta}} \frac{Z_{\boldsymbol{\Delta}}\,e^2}{\Delta}\,\frac{1}{|\hat{\boldsymbol{\Delta}}-\boldsymbol{u}|} \quad , \tag{6.10}$$

where the charge of the ion at position $\boldsymbol{\Delta}$ is $Z_{\boldsymbol{\Delta}}\,e$. The general result, using the spherical harmonic expansion, is

$$V_{\text{CF}}(\boldsymbol{r}) = \sum_{\boldsymbol{\Delta}} \frac{4\pi Z_{\boldsymbol{\Delta}} e^2}{\Delta} \sum_{l=0}^{\infty} \frac{1}{2l+1}\left(\frac{r}{\Delta}\right)^{l} \sum_{m=-l}^{l} Y^*_{lm}(\hat{\boldsymbol{\Delta}})\,Y_{lm}(\hat{\boldsymbol{r}}) \quad . \tag{6.11}$$

In a tetragonal environment, the ions are located at $\boldsymbol{\Delta} = \pm a\,\hat{\boldsymbol{x}}$, $\pm a\,\hat{\boldsymbol{y}}$, and $\pm b\,\hat{\boldsymbol{z}}$. The isotropy of space is

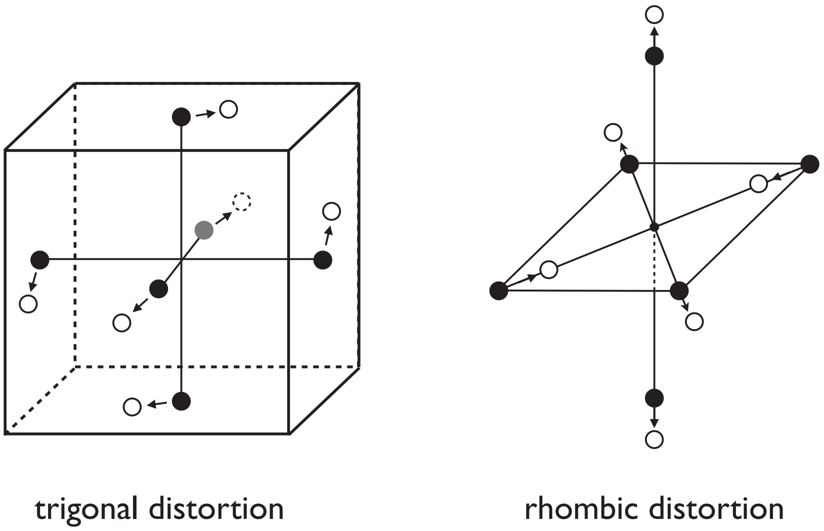

Figure 6.4: Trigonal and rhombic distortions of an octahedral environment.

already broken at $\mathcal{O}(r^2)$ of the expansion, and one finds, neglecting the constant piece,

$$V_{\text{tet}}(\boldsymbol{r}) = \overbrace{-Ze^2\left(\frac{1}{a}-\frac{1}{b}\right)}^{A}\left(\frac{x^2}{a^2}+\frac{y^2}{a^2}-\frac{2z^2}{b^2}\right) \quad . \tag{6.12}$$

Here we have assumed that all the surrounding ions have charge $+Ze$, but the D_{4h} symmetry allows for the planar ions do have a different charge than the axial ions. Note that for $a = b$ the above potential vanishes. In this case the symmetry is cubic and we must go to fourth order. Suppose $Z < 0$ and that $a < b$. In this case the coefficient A is positive, and we see that the p_x and p_y orbitals incur an energy cost, since they are pointed directly toward the closest negative ions. These orbitals provide suitable basis functions for the E IRREP of D_4. The p_z orbital is then lower in energy, as Fig. 6.3 indicates, and corresponds to the A_2 IRREP. For d orbitals, clearly $d_{x^2-y^2}$ is going to be highest in energy, since its lobes are all pointing toward the planar ions. This transforms under the B_1 IRREP, as may be seen by inspection of the characters. The d_{xz} and d_{yz} orbitals clearly remain degenerate, since x may still be rotated into y. Accordingly they transform as the two-dimensional E IRREP. This leaves $d_{3z^2-r^2}$ and d_{xy}. There is no symmetry relating these orbitals, and they transform as the one-dimensional IRREPs A_1 and B_2, respectively.

6.2.4 Cubic and octahedral environments

Now let's implement the same calculation for the case of a cubic or octahedral environment. Centering each about the origin, one has that the eight cubic sites are located at $R\,(\pm 1, \pm 1, \pm 1)$. The six octahedral sites are at $R\left\{(\pm 1, 0, 0)\,,\ (0, \pm 1, 0)\,,\ (0, 0, \pm 1)\right\}$. If the side lengths are all a, then $R = \frac{\sqrt{3}}{2}\,a$ for the cube and $R = \frac{1}{\sqrt{2}}\,a$ for the octrahedron. One finds in each case that the local potential, neglecting the constant

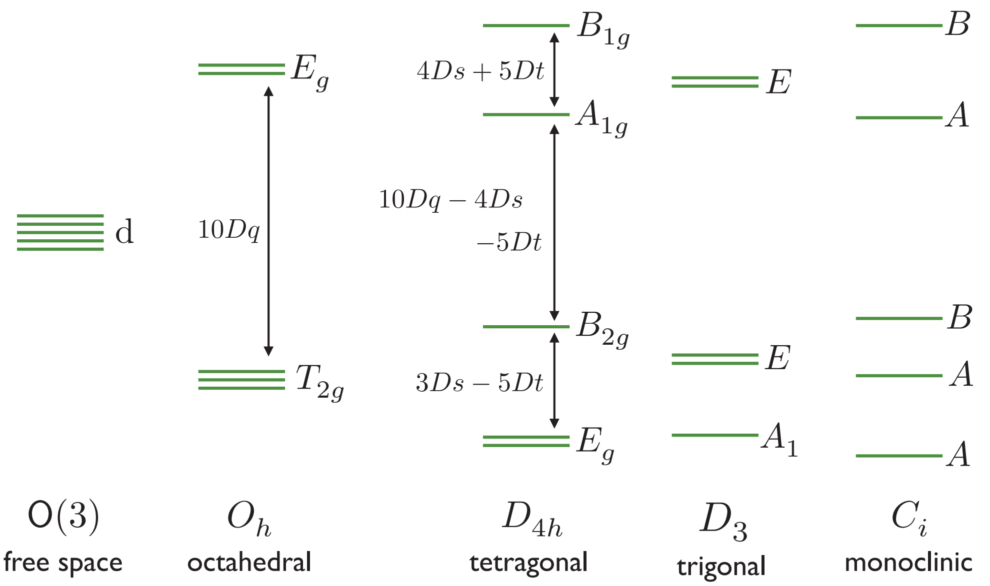

Figure 6.5: Splitting of an atomic d-level in different crystalline environments.

piece, may be written

$$V(\boldsymbol{r})=\frac{A}{R^5}\Big(x^4+y^4+z^4-\tfrac{3}{5}\,r^4\Big) \quad , \tag{6.13}$$

where $A_{\text{cube}}=-\frac{70}{9}Ze^2$ and $A_{\text{octahedron}}=+\frac{35}{4}Ze^2$. Thus, the cubic and octahedral environments have an opposite effect, and crystal field levels pushed up in a cubic environment are pushed down in an octahedral environment, all else being the same. A typical scenario is that our central ion is a transition metal, and the surrounding cage is made of O^{--} ions ($Z=-2$).

Consulting Tab. 6.5, we see that atomic p levels remain threefold degenerate in a cubic or octahedral environment, transforming as the T_2 representation. The fivefold degeneracy of the atomic d level is split, though, into $2^+=E\oplus T_2$. If the site symmetry is O_h, we have $2^+=E_g\oplus T_{2g}$. In a cubic environment, the T_{2g} levels are pulled lower, since the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals point toward the face centers of the cube, *i.e.* away from the oxygen anions, and the E_g levels are pushed up. In an octahedral environment, the situation is reversed.

What happens in a tetragonal environment? Carrying out the above calculation of $V(\boldsymbol{r})$, one finds a nontrivial contribution at third order in $\boldsymbol{r}/R$, and

$$V_{\text{tet}}(\boldsymbol{r})=\frac{A}{R^4}\,xyz \quad , \tag{6.14}$$

with $A=-\frac{20}{\sqrt{3}}Ze^2$. Notice how in all cases the potential transforms according to the trivial representation $\varGamma_1$. The decomposition of the 2^+ IRREP of O(3) into IRREPs of T_d is pretty much identical, because T_d and O are isomorphic. One again has $2^+=E\oplus T_2$. With respect to the 12 element group T, one has $s^+=E\oplus T$. Tab. 6.6 indicates how electron shell levels up to $l=4$ split in various crystal field environments. Note again how there is no g or u index on the IRREPs of the proper point groups, since they do not contain the inversion element I.

We can compute analytically the energy shifts using the point charge model. For the case of an atomic d level, we first resolve the d states into combinations transforming according to the E and T_2 IRREPs of O, writing the angular wavefunctions as

$$\begin{aligned} d_{xy}(\hat{\boldsymbol{r}}) &= \tfrac{i}{\sqrt{2}}\Big\{Y_{2,-2}(\hat{\boldsymbol{r}}) - Y_{2,2}(\hat{\boldsymbol{r}})\Big\} \\ d_{yz}(\hat{\boldsymbol{r}}) &= \tfrac{1}{\sqrt{2}}\Big\{Y_{2,-1}(\hat{\boldsymbol{r}}) + Y_{2,1}(\hat{\boldsymbol{r}})\Big\} \\ d_{xz}(\hat{\boldsymbol{r}}) &= \tfrac{i}{\sqrt{2}}\Big\{Y_{2,-1}(\hat{\boldsymbol{r}}) - Y_{2,1}(\hat{\boldsymbol{r}})\Big\} \quad , \end{aligned} \tag{6.15}$$

which transform as T_2, and

$$\begin{aligned} d_{x^2-y^2}(\hat{\boldsymbol{r}}) &= \tfrac{1}{\sqrt{2}}\Big\{Y_{2,-2}(\hat{\boldsymbol{r}}) + Y_{2,2}(\hat{\boldsymbol{r}})\Big\} \\ d_{3z^2-r^2}(\hat{\boldsymbol{r}}) &= Y_{2,0}(\hat{\boldsymbol{r}}) \quad , \end{aligned} \tag{6.16}$$

which transform as E. According to the Wigner-Eckart theorem, this already diagonalizes the 5×5 Hamiltonian within the atomic d basis, with

$$\varepsilon(E_g) = \big\langle\, d_{x^2-y^2} \,\big|\, V(\boldsymbol{r}) \,\big|\, d_{x^2-y^2} \,\big\rangle \qquad , \qquad \varepsilon(T_{2g}) = \big\langle\, d_{xy} \,\big|\, V(\boldsymbol{r}) \,\big|\, d_{xy} \,\big\rangle \quad . \tag{6.17}$$

One finds $\varepsilon^{\rm OCT}(E_g) = -4Dq$ and $\varepsilon^{\rm OCT}(T_{2g}) = +6Dq$, with

$$Dq = \frac{eq\,\langle r^4\rangle}{6a^5} \quad , \tag{6.18}$$

where $q = Ze$ is the ligand charge, a is the distance from the metal ion (where the d electrons live) to the ligand ions, and $\langle r^4\rangle = \langle\, R_{n2} \,|\, r^4 \,|\, R_{n2} \,\rangle$ is the expectation of r^4 with respect to the radial wavefunction $R_{nl}(r)$ with $l = 2$. For the cubic environment, one finds $\varepsilon^{\rm CUB}(E_g) = -\frac{8}{9}\times 6Dq$ and $\varepsilon^{\rm CUB}(T_{2g}) = +\frac{8}{9}\times 4Dq$, while in a tetrahedral environment $\varepsilon^{\rm THD}(E_g) = -\frac{4}{9}\times 6Dq$ and $\varepsilon^{\rm THD}(T_{2g}) = +\frac{4}{9}\times 4Dq$. In a tetragonal environment, one finds

$$\begin{aligned} \varepsilon^{\rm TTR}(E_g) &= -4Dq - Ds + 4Dt \\ \varepsilon^{\rm TTR}(B_{2g}) &= -4Dq + 2Ds - Dt \\ \varepsilon^{\rm TTR}(A_{1g}) &= 6Dq - 2Ds - 6Dt \\ \varepsilon^{\rm TTR}(B_{1g}) &= 6Dq + 2Ds - Dt \quad , \end{aligned} \tag{6.19}$$

where

$$Ds = \frac{2eq}{7}\bigg(\frac{1}{a^3} - \frac{1}{b^3}\bigg)\langle r^2\rangle \qquad , \qquad Dt = \frac{2eq}{21}\bigg(\frac{1}{a^5} - \frac{1}{b^5}\bigg)\langle r^4\rangle \quad . \tag{6.20}$$

Fig. 6.5 gives a schematic picture of how an atomic d level splits in various crystalline environments ($D > 0$ case is shown).

6.2.5 Matrix elements and selection rules

Recall the Wigner-Eckart theorem,

$$\big\langle\, \varGamma_c\, \gamma \,,\, l_c \,\big|\, \hat{Q}^{\varGamma_a}_{\alpha} \,\big|\, \varGamma_b\, \beta \,,\, l_b \,\big\rangle = \sum_s \left(\begin{matrix} \varGamma_a & \varGamma_b \\ \alpha & \beta \end{matrix}\,\middle|\,\begin{matrix} \varGamma_c \,,\, s \\ \gamma \end{matrix}\right) \big\langle\, \varGamma_c \,,\, l_c \,\big\|\, \hat{Q}^{\varGamma_a} \,\big\|\, \varGamma_b \,,\, l_b \,\big\rangle_s \quad , \tag{6.21}$$

L^η	O_h cubic	T_d tetrahedral	D_{4h} tetragonal	D_3 trigonal	D_{2h} orthorhombic
0^+ (s)	A_{1g}	A_1	A_{1g}	A_1	A_{1g}
1^- (p)	T_{1u}	T_2	$A_{2u} \oplus E_u$	$A_2 \oplus E$	$B_{2u} \oplus E_u$
2^+ (d)	$E_g \oplus T_{2g}$	$E \oplus T_2$	$A_{1g} \oplus B_{1g}$ $\oplus B_{2g} \oplus E_g$	$A_1 \oplus 2E$	$A_{1g} \oplus B_{1g}$ $\oplus B_{2g} \oplus E_g$
3^- (f)	$A_{2u} \oplus T_{1u} \oplus T_{2u}$	$A_2 \oplus T_1 \oplus T_2$	$A_{2u} \oplus B_{1u}$ $\oplus B_{2u} \oplus 2E_u$	$A_1 \oplus 2A_2$	$A_{1u} \oplus A_{2u}$ $\oplus B_{2u} \oplus 2E_u$
4^+ (g)	$A_{1g} \oplus E_g$ $\oplus T_{1g} \oplus T_{2g}$	$A_1 \oplus E$ $\oplus T_1 \oplus T_2$	$2A_{1g} \oplus A_{2g} \oplus B_{1g}$ $\oplus B_{2g} \oplus 2E_g$	$2A_1 \oplus A_2 \oplus 3E$	$2A_{1g} \oplus A_{2g} \oplus B_{1g}$ $\oplus B_{2g} \oplus 2E_g$

Table 6.6: Splitting of one-electron levels in crystal fields of different symmetry.

where $l_{b,c}$ labels different subspaces transforming according to the $\Gamma_{b,c}$ IRREPs of the symmetry group G, and s is the multiplicity index necessary when G is not simply reducible. Operators $\hat{Q}$ such as the Hamiltonian transform according to the trivial representation, in which case

$$\big\langle\, \Gamma_c\,\gamma\,,\, l_c \,\big|\, \hat{Q} \,\big|\, \Gamma_b\,\beta\,,\, l_b \,\big\rangle = \delta_{\Gamma_b\,\Gamma_c}\,\delta_{\beta\gamma}\,\big\langle\, \Gamma_c\,,\, l_c \,\big\|\, \hat{Q} \,\big\|\, \Gamma_b\,,\, l_b \,\big\rangle \quad , \tag{6.22}$$

where

$$\big\langle\, \Gamma_c\,,\, l_c \,\big\|\, \hat{Q} \,\big\|\, \Gamma_b\,,\, l_b \,\big\rangle = \frac{1}{d_{\Gamma_b}} \sum_\beta \big\langle\, \Gamma_b\,\beta\,,\, l_c \,\big|\, \hat{Q} \,\big|\, \Gamma_b\,\beta\,,\, l_b \,\big\rangle \quad . \tag{6.23}$$

In order that $\left(\begin{smallmatrix} \Gamma_a & \Gamma_b \\ \alpha & \beta \end{smallmatrix} \middle| \begin{smallmatrix} \Gamma_c\,, s \\ \gamma \end{smallmatrix}\right) \neq 0$, we must have $\Gamma_c \subset \Gamma_a \times \Gamma_b$, *i.e.*

$$n_{\Gamma_c}(\Gamma_a \times \Gamma_b) = \frac{1}{N_G} \sum_{\mathcal{C}} N_{\mathcal{C}}\, \chi^{\Gamma_c^*}(\mathcal{C})\, \chi^{\Gamma_a}(\mathcal{C})\, \chi^{\Gamma_b}(\mathcal{C}) \tag{6.24}$$

must be nonzero. Equivalently, the condition may be stated as $\Gamma_b \subset \Gamma_a^* \times \Gamma_c$ or $\Gamma_a \subset \Gamma_b^* \times \Gamma_c$.

Let's apply these considerations to the problem of radiative transitions in atoms. We follow the treatment in chapter 3 of Lax, following a brief review of quantum radiation theory. The single electron Hamiltonian is

$$\hat{H} = \frac{1}{2m}\Big(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\Big)^2 + V(\boldsymbol{r}) + g\mu_{\rm B}\boldsymbol{H}\cdot\boldsymbol{s}/\hbar + \frac{1}{2m^2c^2}\,\boldsymbol{s}\cdot\boldsymbol{\nabla}V \times \big(\boldsymbol{p} + \tfrac{e}{c}\boldsymbol{A}\big) \quad , \tag{6.25}$$

where $\boldsymbol{A}$ is the vector potential of the electromagnetic field, $V(\boldsymbol{r})$ is the scalar potential due to the ionic nucleus, and $\boldsymbol{s} = \frac{1}{2}\hbar\boldsymbol{\sigma}$ is the electron spin operator. $\mu_{\rm B} = \frac{e\hbar}{2mc} = 5.788 \times 10^{-9}$ eV/G is the Bohr magneton, and $g = 2 + \frac{\alpha}{\pi} + \mathcal{O}(\alpha^2)$ with $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the so-called g-factor[5], which is $g = 2$ at "tree level" within

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[5] Like, duh.

	E	C_2	C_3	C_4	C_6	I	σ	S_6	S_4	S_3
1^- ($\boldsymbol{P}$)	3	−1	0	1	2	−3	1	0	−1	−2
1^+ ($\boldsymbol{M}$)	3	−1	0	1	2	3	−1	0	1	2

Table 6.7: Characters for the electric and magnetic dipole operators.

quantum electrodynamics[6]. The last term above is due to the spin-orbit interaction and we will neglect the contribution of $\boldsymbol{A}$ therein. The quantized electromagnetic field is described by the vector potential[7]

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{2\pi\hbar c}{V|\boldsymbol{k}|}} \Big(a_{\boldsymbol{k}\lambda}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, \hat{\boldsymbol{e}}^*_\lambda(\boldsymbol{k}) + a^\dagger_{\boldsymbol{k}\lambda}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, \hat{\boldsymbol{e}}_\lambda(\boldsymbol{k}) \Big) \quad , \tag{6.26}$$

where $\hat{\boldsymbol{e}}_\lambda(\boldsymbol{k})$ is the polarization vector, with $\big\{ \hat{\boldsymbol{e}}_1(\boldsymbol{k}) \, , \, \hat{\boldsymbol{e}}_2(\boldsymbol{k}) \, , \, \hat{\boldsymbol{k}} \big\}$ an orthonormal triad for each $\boldsymbol{k}$.

The matrix element one must compute is that of $\boldsymbol{p} \cdot \boldsymbol{A}(\boldsymbol{r})$, where $\boldsymbol{p}$ is the electron momentum and $\boldsymbol{A}(\boldsymbol{r})$ is the quantized electromagnetic vector potential. Writing $\boldsymbol{A}(\boldsymbol{r})$ as the above Fourier sum, we need to evaluate

$$\big\langle\, 0 \,\big|\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, \boldsymbol{p} \cdot \hat{\boldsymbol{e}}^*_\lambda(\boldsymbol{k}) \,\big|\, n \,\big\rangle \quad , \tag{6.27}$$

where the atomic transition is from $|\, n \,\rangle$ to the ground state $|\, 0 \,\rangle$, $\boldsymbol{k}$ is the wavevector of the emitted photon, and $\hat{\boldsymbol{e}}_\lambda(\boldsymbol{k})$ is the photon polarization vector (with λ the polarization index). If $ka_{\rm B} \ll 1$, we may approximate $e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \approx 1$, and we then need the matrix element of

$$\hat{\boldsymbol{e}}^*_\lambda(\boldsymbol{k}) \cdot \langle\, 0 \,|\, \boldsymbol{p} \,|\, n \,\rangle = \frac{m}{i\hbar}\, (E_n - E_0)\, \hat{\boldsymbol{e}}^*_\lambda(\boldsymbol{k}) \cdot \langle\, 0 \,|\, \boldsymbol{r} \,|\, n \,\rangle \quad . \tag{6.28}$$

If the states $|\, 0 \,\rangle$ and $|\, n \,\rangle$ are of the same parity, then the transition is forbidden within the electric dipole approximation, and one must expand $\exp(-i\boldsymbol{k}\cdot\boldsymbol{r}) = 1 - i\boldsymbol{k}\cdot\boldsymbol{r} - \frac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{r})^2 + \ldots$ to next order, *i.e.* to the magnetic dipole and electric quadrupole terms. Magnetic dipole transitions involve the matrix element $\boldsymbol{k} \times \hat{\boldsymbol{e}}^*_\lambda(\boldsymbol{k}) \cdot \langle\, 0 \,|\, \boldsymbol{l} + 2\boldsymbol{s} \,|\, n \,\rangle$, where $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$ and $\boldsymbol{s}$ is the electron spin. Summing over all the electrons in the unfilled shell, we have the electric and magnetic dipole operators,

$$\boldsymbol{P} = e \sum_i \boldsymbol{r}_i \qquad , \qquad \boldsymbol{M} = \frac{e\hbar}{2mc} \sum_i (\boldsymbol{l}_i + 2\boldsymbol{s}_i) \quad . \tag{6.29}$$

We see that these operators transform as an axial vector ($\boldsymbol{P}$, or 1^-) and a pseudovector ($\boldsymbol{M}$, or 1^+), respectively. This has profound consequences for the allowed matrix elements.

Site group C_{3v}

Lax[8] considers the case of an ion in an environment with a C_{3v} site group. The characters for the vector and pseudovector representations of the $\boldsymbol{P}$ and $\boldsymbol{M}$ operators are given in Tab. 6.7. Consulting the

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[6] Radiative corrections to $g_{\rm tree} = 2$ may be cast in the form of an asymptotic power series in the fine structure constant $\alpha = e^2/\hbar c \approx \frac{1}{137}$.

[7] See, *e.g.*, J. J. Sakurai, *Advanced Quantum Mechanics*, §2.3.

[8] See the subsection "Dipole Radiation Selection Rules" on pp. 88-89 in Lax, *Symmetry Principles*.

character table for C_{3v} (Tab. 2.1), we decompose their respective $\mathsf{O}(3)$ IRREPs $1^{\mp}$ into C_{3v} IRREPs, and find $1^- = A_1 \oplus E$ and $1^+ = A_2 \oplus E$, with P_z transforming as A_1 and $P_{x,y}$ as E. Similarly, M_z transforms as A_2 and $M_{x,y}$ as E. We now need to know how the products of the C_{3v} IRREPs decompose, which is summarized in Tab. 6.9. Since $A_1 \times A_2 = A_2 \times A_1 = A_2$, and we see that no component of $\boldsymbol{P}$ can have a nonzero matrix elements between these corresponding IRREPs, *i.e.* $\langle\, A_1 \,|\, \boldsymbol{P} \,|\, A_2 \,\rangle = 0$. Similarly, since $A_1 \times A_1 = A_2 \times A_2 = A_1$, we have $\langle\, A_1 \,|\, \boldsymbol{M} \,|\, A_1 \,\rangle = \langle\, A_2 \,|\, \boldsymbol{M} \,|\, A_2 \,\rangle = 0$. Further restrictions apply when we consider the longitudinal (Q_z) and transverse ($Q_{x,y}$) parts of these operators, and we find that $\langle\, A_i \,|\, Q_z \,|\, E \,\rangle = \langle\, A_i \,|\, Q_{x,y} \,|\, A_j \,\rangle = 0$ where $\boldsymbol{Q}$ is either $\boldsymbol{P}$ or $\boldsymbol{M}$, for all i and j.

Site group D_{3d}

Now consider the problem of dipole radiation in a D_{3d} environment. haracter table for D_{3d}, including the decomposition of the $\boldsymbol{P}$ and $\boldsymbol{M}$ representations, is provided in Tab. 6.8. Unlike C_{3v} , the group D_{3d} contains the inversion I, hence its IRREPs are classified as either g or u, according to whether $\chi^{\Gamma}(I) = \pm d_{\Gamma}$. From Tab. 6.8, we find $1^- = A_{2u} \oplus E_u$ and $1^+ = A_{2g} \oplus E_g$. Next, we decompose the products of the D_{3d} IRREPs, in Tab. 6.9, and we obtain $1^- = A_{2u} \oplus E_u$ and $1^+ = A_{2g} \oplus E_g$. Since I commutes with all group elements, its eigenvalue is a good quantum number, and accordingly $\langle\, \Gamma_g \,|\, \boldsymbol{M} \,|\, \Gamma'_u \,\rangle = 0$ for any IRREPs Γ_g and Γ'_u , since $\boldsymbol{M}$ is even under inversion and can have no finite matrix element between states of different parity. Similarly, $\boldsymbol{P}$ is odd under inversion, so $\langle\, \Gamma_g \,|\, \boldsymbol{P} \,|\, \Gamma'_g \,\rangle = \langle\, \Gamma_u \,|\, \boldsymbol{P} \,|\, \Gamma'_u \,\rangle = 0$. Again, matrix elements of the longitudinal and transverse components are subject to additional restrictions, and the general rule is that some IRREP Γ_a contained in the decomposition of a given operator $\hat{Q}$ must also be contained in the decomposition of the product representation $\Gamma^*_b \times \Gamma_c$ in order that $\langle\, \Gamma_c \,|\, \hat{Q} \,|\, \Gamma_b \,\rangle$ be nonzero[9].

D_{3d}	E	$2C_3$	$3C'_2$	I	$2IC_3$	$3IC'_2$	
A_{1g}	1	1	1	1	1	1	
A_{2g}	1	1	-1	1	1	-1	
E_g	2	-1	0	2	-1	0	
A_{1u}	1	1	1	-1	-1	-1	
A_{2u}	1	1	-1	-1	-1	1	
E_u	2	-1	0	-2	1	0	
1^- ($\boldsymbol{P}$)	3	0	-1	-3	0	1	$A_{2u} \oplus E_u$
1^+ ($\boldsymbol{M}$)	3	0	-1	3	0	-1	$A_{2g} \oplus E_g$

Table 6.8: Character table for D_{3d}.

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[9] Note how we are using an abbreviated notation $|\, \Gamma \,\rangle$ for the more complete $|\, \Gamma\, \mu\, , l\,\rangle$.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 \oplus A_2 \oplus E$

D_{3d}	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
A_{1g}	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
A_{2g}	A_{2g}	A_{1g}	E_g	A_{2u}	A_{1u}	E_u
E_g	E_g	E_g	$A_{1g} \oplus A_{2g} \oplus E_g$	E_u	E_u	$A_{1u} \oplus A_{2u} \oplus E_u$
A_{1u}	A_{1u}	A_{2u}	E_u	A_{1g}	A_{2g}	E_g
A_{2u}	A_{2u}	A_{1u}	E_u	A_{2g}	A_{1g}	E_g
E_u	E_u	E_u	$A_{1u} \oplus A_{2u} \oplus E_u$	E_g	E_g	$A_{1g} \oplus A_{2g} \oplus E_g$

Table 6.9: Decomposition of products of IRREPs in C_{3v} and D_{3d}. Red entries indicate cases where $\langle\, \mathit{\Gamma} \,|\, \boldsymbol{P} \,|\, \mathit{\Gamma}' \,\rangle = 0$ for all components of $\boldsymbol{P}$, and blue entries where $\langle\, \mathit{\Gamma} \,|\, \boldsymbol{M} \,|\, \mathit{\Gamma}' \,\rangle = 0$ for all components of $\boldsymbol{M}$, where $\mathit{\Gamma}$ and $\mathit{\Gamma}'$ are the row and column IRREP labels, respectively. Additional constraints apply to matrix elements of the longitudinal (z) and transverse (x, y) components individually (see text).

6.2.6 Crystal field theory with spin

Thus far we have considered how the $2l + 1$ states in a single-electron orbital of angular momentum l, which form an IRREP of $\mathsf{O}(3)$, split in the presence of a crystal field and reorganize into IRREPs of the local site group, according to Eqn. 6.1. This formalism may be applied to many-electron states described by terms ${}^{2S+1}L_J$, provided $J \in \mathbb{Z}$. Or it may be applied to terms on the basis of their L values alone, if we neglect the atomic spin-orbit coupling which is the basis of Hund's third rule. In this section, we consider term splitting in more detail, exploring how it can be approached either from the strong spin-orbit coupling side or the strong crystal field potential side. We shall show how a given term ${}^{2S+1}L_J$ may be analyzed by either of the following procedures:

(i) First decompose the spin S and angular momentum L multiplets into IRREPs $\mathit{\Gamma}_a(S)$ and $\mathit{\Gamma}_b(L)$ of $\mathcal{P}(\boldsymbol{r})$, respectively. Then decompose the products $\mathit{\Gamma}_a(S) \times \mathit{\Gamma}_b(L)$, again into IRREPs of $\mathcal{P}(\boldsymbol{r})$. This is appropriate when $V_{\rm CF} \gg V_{\rm RS}$, where $V_{\rm CF}$ is the scale of the crystal field potential, and $V_{\rm RS}$ the scale of the atomic Russell-Saunders L-S coupling.

(ii) First decompose ${}^{2S+1}L$ within $\mathsf{O}(3)$ into IRREPs according to their total angular momentum J. Then decompose these $\mathsf{O}(3)$ IRREPs into IRREPs of $\mathcal{P}(\boldsymbol{r})$. This is appropriate when $V_{\rm RS} \gg V_{\rm CF}$.

We illustrate the salient features by means of two examples.

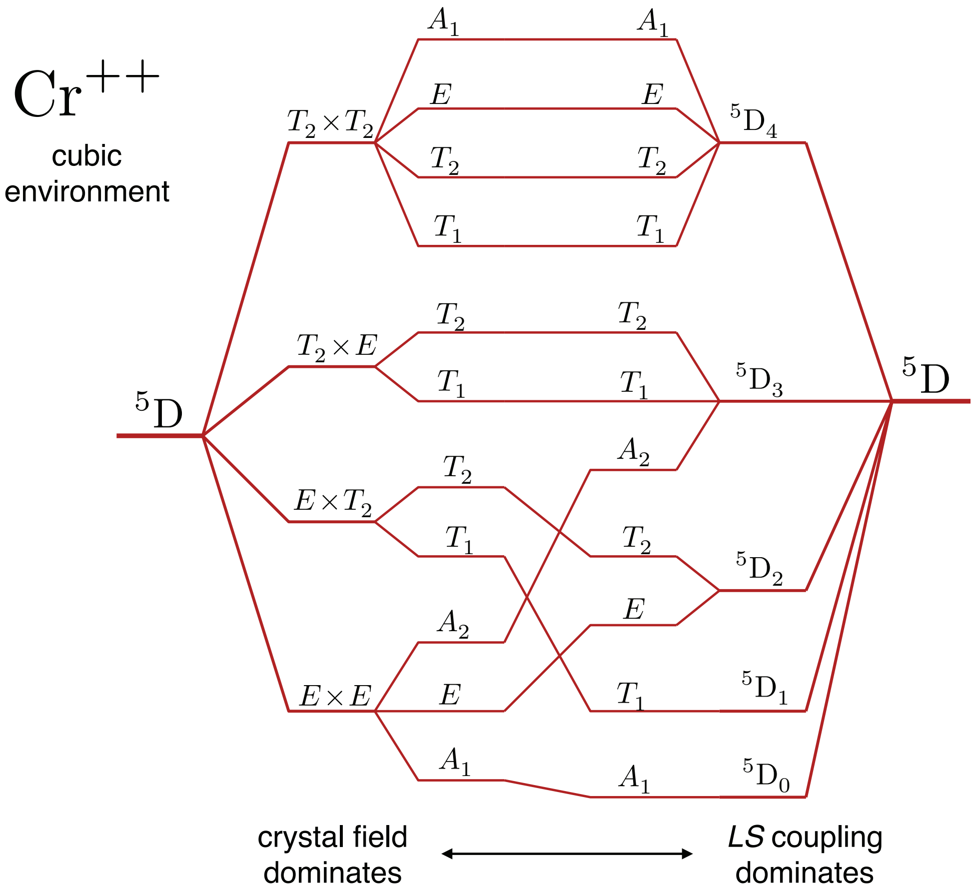

Figure 6.6: Decomposition of the ^{5}D states of Cr^{++} into IRREPs of O.

Cr^{++} in a cubic environment

The first is that of the Cr^{++} ion, whose electronic configuration is $[\mathrm{Ar}]\,4\mathrm{s}^0\,3\mathrm{d}^4$. The ground state term in free space is $^5\mathrm{D}_0$, *i.e.* $S = L = 2$. According to Tab. 6.5, each of these degenerate multiplets, for both spin and angular momentum, decomposes as $\mathrm{D} = E \oplus T_2$ within O. Thus,

$$^5\mathrm{D} = \varGamma_{S=2} \times \varGamma_{L=2} = \big(E \oplus T_2\big) \times \big(E \oplus T_2\big) = E \times E \;\oplus\; E \times T_2 \;\oplus\; T_2 \times E \;\oplus\; T_2 \times T_2 \quad . \tag{6.30}$$

Appealing again to the character table for O, from Eqn. 6.1 we compute

$$\begin{aligned} E \times E &= A_1 \oplus A_2 \oplus E \\ E \times T_2 = T_2 \otimes E &= T_1 \oplus T_2 \\ T_2 \times T_2 &= A_1 \oplus E \oplus T_1 \oplus T_2 \quad . \end{aligned} \tag{6.31}$$

The resulting tally of O IRREPs and their multiplicities:

$$^5\mathrm{D} = 2\,A_1 \oplus A_2 \oplus 2\,E \oplus 3\,T_1 \oplus 3\,T_2 \quad . \tag{6.32}$$

T_d'	E	$\overline{E}$	$8C_3$	$8\overline{C}_3$	$3C_2$ $3\overline{C}_2$	$6S_4$	$6\overline{S}_4$	$6\sigma_d$ $6\overline{\sigma}_d$		
O'	E	$\overline{E}$	$8C_3$	$8\overline{C}_3$	$3C_2$ $3\overline{C}_2$	$6C_4$	$6\overline{C}_4$	$6C_2'$ $6\overline{C}_2'$	O' basis	T_d' basis
$\Delta_1 = A_1$	1	1	1	1	1	1	1	1	r^2	r^2 or xyz
$\Delta_2 = A_2$	1	1	1	1	1	-1	-1	-1	xyz	$L_x\,L_y\,L_z$
$\Delta_{12} = E$	2	2	-1	-1	2	0	0	0	$\{\sqrt{3}\,(x^2{-}y^2)\,,3z^2{-}r^2\}$	$\{\sqrt{3}\,(x^2{-}y^2)\,,3z^2{-}r^2\}$
$\Delta_{15} = T_1$	3	3	0	0	-1	1	1	-1	$\{L_x\,,L_y\,,L_z\}$	$\{L_x\,,L_y\,,L_z\}$
$\Delta_{25} = T_2$	3	3	0	0	-1	-1	-1	1	$\{yz\,,\,zx\,,\,xy\}$	$\{x\,,y\,,z\}$
Δ_6	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0	$\{\,\lvert\,\frac{1}{2}\,,\,\pm\frac{1}{2}\,\rangle\}$	$\{\,\lvert\,\frac{1}{2}\,,\,\pm\frac{1}{2}\,\rangle\}$
Δ_7	2	-2	1	-1	0	$-\sqrt{2}$	$\sqrt{2}$	0	$\{xyz\otimes\lvert\,\frac{1}{2}\,,\,\pm\frac{1}{2}\,\rangle\}$	$\{L_x\,L_y\,L_z\otimes\lvert\,\frac{1}{2}\,,\,\pm\frac{1}{2}\,\rangle\}$
Δ_8	4	-4	-1	1	0	0	0	0	$\{\,\lvert\,\frac{3}{2}\,,\,m\,\rangle\}$	$\{\,\lvert\,\frac{3}{2}\,,\,m\,\rangle\}$
$\mathit{\Gamma}_{1/2}$	2	-2	1	-1	0	$\sqrt{2}$	$-\sqrt{2}$	0	Δ_6	
$\mathit{\Gamma}_{3/2}$	4	-4	-1	1	0	0	0	0	Δ_8	
$\mathit{\Gamma}_{5/2}$	6	-6	0	0	0	$-\sqrt{2}$	$\sqrt{2}$	0	$\Delta_7 \oplus \Delta_8$	
$\mathit{\Gamma}_{7/2}$	8	-8	1	-1	0	0	0	0	$\Delta_6 \oplus \Delta_7 \oplus \Delta_8$	
$\mathit{\Gamma}_{9/2}$	10	-10	-1	1	0	$\sqrt{2}$	$-\sqrt{2}$	0	$\Delta_6 \oplus 2\,\Delta_8$	
$\Delta_8 \times \Delta_2$	4	-4	-1	1	0	0	0	0	Δ_8	
$\Delta_8 \times \Delta_{15}$	12	-12	0	0	0	0	0	0	$\Delta_6 \oplus \Delta_7 \oplus 2\,\Delta_8$	
$\Delta_8 \times \Delta_{25}$	12	-12	0	0	0	0	0	0	$\Delta_6 \oplus \Delta_7 \oplus 2\,\Delta_8$	

Table 6.10: Character table for the double groups O' and T_d'.

Note that a sum of their dimensions yields $2 + 1 + 4 + 9 + 9 = 25$, which of course is consistent with $S = 2$ and $L = 2$. Now let's approach this from the spin-orbit side. That is, we first multiply the $S = 2$ and $L = 2$ IRREPs within O(3), yielding

$$2 \times 2 = 0 \oplus 1 \oplus 2 \oplus 3 \oplus 4 \quad . \tag{6.33}$$

A check of the bottom half of Tab. 6.5 reveals that this once again results in the same final tally of O IRREPs. This situation is illustrated in Fig. 6.6.

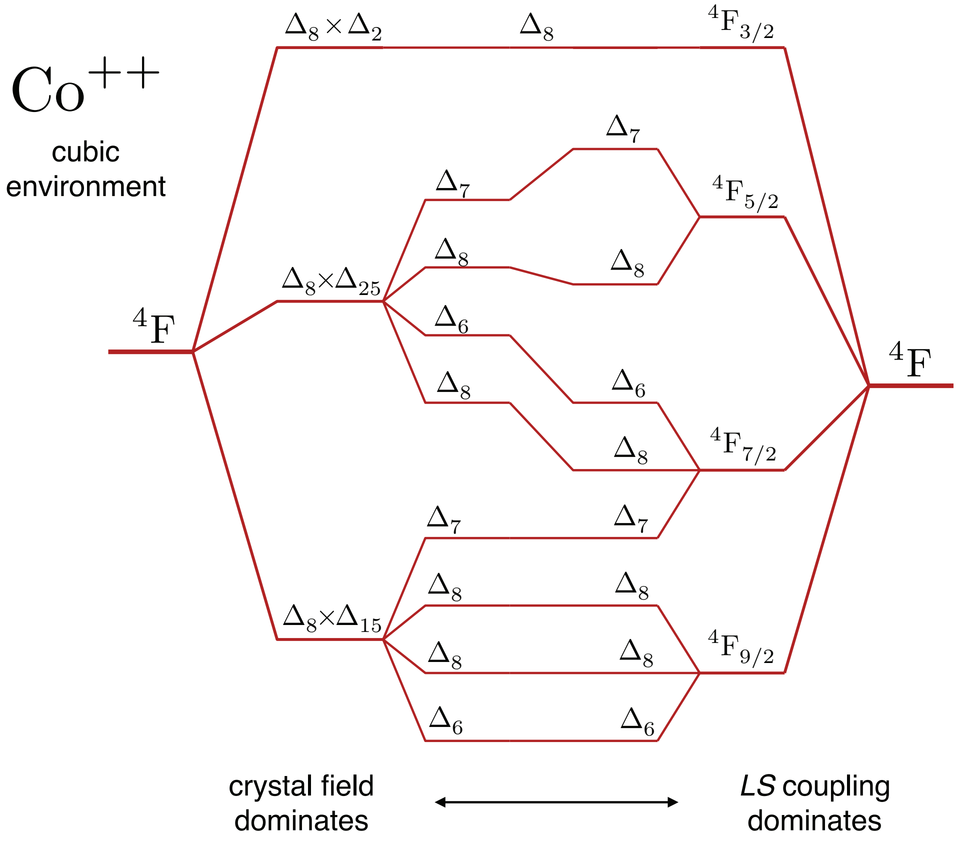

Figure 6.7: Decomposition of the ^{4}F states of Co^{++} into IRREPs of the double group O'.

Co^{++} in a cubic environment

Next, consider the case of Co^{++}, whose ground state term is $^4\mathrm{F}_{9/2}$, corresponding to $S = \frac{3}{2}$ and $L = 3$. We first ignore spin-orbit, and we decompose the $L = 3$ multiplet of O(3) as $\mathrm{F} = A_2 \oplus T_1 \oplus T_2$. We adopt the alternate labels Δ_2, Δ_{15}, and Δ_{25} for these IRREPs of O (see Tab. 6.10[10]) because we will need to invoke the double group O' and its IRREPs presently. We next decompose the $S = \frac{3}{2}$ spin component, and here is where we need the double group O' and its IRREPs. We see from the table that $\Gamma_{3/2} = \Delta_8$. We now must decomposing the product representations of the double group O', and we find

$$\begin{aligned} \Delta_8 \times \Delta_2 &= \Delta_8 \\ \Delta_8 \times \Delta_{15} &= \Delta_6 \oplus \Delta_7 \oplus 2\,\Delta_8 \\ \Delta_8 \times \Delta_{25} &= \Delta_6 \oplus \Delta_7 \oplus 2\,\Delta_8 \quad . \end{aligned} \tag{6.34}$$

Therefore we conclude

$$^4\mathrm{F} = 2\,\Delta_6 \oplus 2\,\Delta_7 \oplus 5\,\Delta_8 \quad . \tag{6.35}$$

Since Δ_6 and Δ_7 are two-dimensional, and Δ_8 is four-dimensional, the total dimension of all the terms in ^{4}F is $2 \times 2 + 2 \times 2 + 4 \times 5 = 28 = (2S + 1)(2L + 1)$, with $S = \frac{3}{2}$ and $L = 3$.

---

[10] Tab. 3.6.2 on p. 95 of Lax contains a rare error: $\chi^{\Gamma_{5/2}}(6C_4) = -\sqrt{2}$ while $\chi^{\Gamma_{9/2}}(6C_4) = +\sqrt{2}$.

Had we first decomposed into $\mathsf{O}(3)$ IRREPs, writing

$$\tfrac{3}{2} \times 3 = \tfrac{3}{2} \oplus \tfrac{5}{2} \oplus \tfrac{7}{2} \oplus \tfrac{9}{2} \quad , \tag{6.36}$$

and decomposing these half-odd-integer spin IRREPs of $\mathsf{O}(3)$ into double group IRREPs of O', we have

$$\begin{aligned} \mathit{\Gamma}_{3/2} &= \Delta_8 \\ \mathit{\Gamma}_{5/2} &= \Delta_7 \oplus \Delta_8 \\ \mathit{\Gamma}_{7/2} &= \Delta_6 \oplus \Delta_7 \oplus \Delta_8 \\ \mathit{\Gamma}_{9/2} &= \Delta_6 \oplus 2\,\Delta_8 \quad . \end{aligned} \tag{6.37}$$

Again we arrive at the same crystal field levels as in Eqn. 6.35, now labeled by IRREPs of the double group O'. The agreement between the two procedures is shown in Fig. 6.7.

Figs. 6.6 and 6.7 are not intended to convey an accurate ordering of energy levels, although in each case the ground state ${}^{2S+1}L_J$ term is placed on the bottom right. Due to level repulsion (see §3.2.6), multiplets corresponding to the same IRREP cannot cross as the ratio of $V_{\rm CF}$ to $V_{\rm RS}$ is varied. Note how in Fig. 6.6 there is level crossing, but between different IRREPs.

Dominant crystal field

We have seen how accounting for crystal field splittings either before or after accounting for spin-orbit coupling yields the same set of levels classified by IRREPs of the local site group. Our starting point in both cases was the partial term ${}^{2S+1}L$, where S and L are obtained from Hund's first and second rules, respectively. Phenomenologically, we can think of Hund's first rule as minimizing the intraatomic ferromagnetic exchange energy $-J_{\rm H}\,\boldsymbol{S}^2$, where $\boldsymbol{S}$ is the total atomic spin. What happens, though, if $V_{\rm CF}$ is so large that it dominates the energy scale $J_{\rm H}$? Consider, for example, the case of Co^{4+}, depicted in Fig. 6.8. The electronic configuration is $[\mathrm{Ar}]\,4\mathrm{s}^0\,4\mathrm{d}^5$, and according to Hund's rules the atomic ground state term is ${}^6\mathrm{S}_{5/2}$. In a weak crystal field, this resolves into IRREPs of O' according to Tab. 6.10 : $\mathit{\Gamma}_{5/2} = \Delta_7 \oplus \Delta_8$, each multiple of which consists of linear combinations of the original $J = S = \frac{5}{2}$ atomic levels. As shown in the figure, there are three electrons in the T_2 orbital and two in the E orbital. The strong Hund's rules coupling $J_{\rm H}$ keeps the upper two electrons from flipping and falling into the lower single particle states. This is the *high spin state*. If $V_{\rm CF} \gg J_{\rm H}$, though, the E electrons cannot resist the energetic advantage of the T_2 states, and the electrons reorganize into the *low spin state*, with $S = \frac{1}{2}$. Unlike the high spin state, the low spin state cannot be written as a linear combination of states from the original ground state term. Rather, one must start with the configuration, which contains $\binom{10}{5} = 252$ states. After some tedious accounting, one finds these states may be resolved into the following $\mathsf{O}(3)$ product representations

$$\begin{aligned} [\mathrm{Ar}]\,4\mathrm{s}^0\,4\mathrm{d}^5 = {}^2\mathrm{I} \oplus {}^2\mathrm{H} \oplus {}^4\mathrm{G} \oplus {}^2\mathrm{G} \oplus {}^2\mathrm{G} \oplus {}^4\mathrm{F} \oplus {}^2\mathrm{F} \oplus {}^2\mathrm{F} \\ \oplus\, {}^4\mathrm{D} \oplus {}^2\mathrm{D} \oplus {}^2\mathrm{D} \oplus {}^2\mathrm{D} \oplus {}^4\mathrm{P} \oplus {}^2\mathrm{P} \oplus {}^6\mathrm{S} \oplus {}^2\mathrm{S} \quad . \end{aligned} \tag{6.38}$$

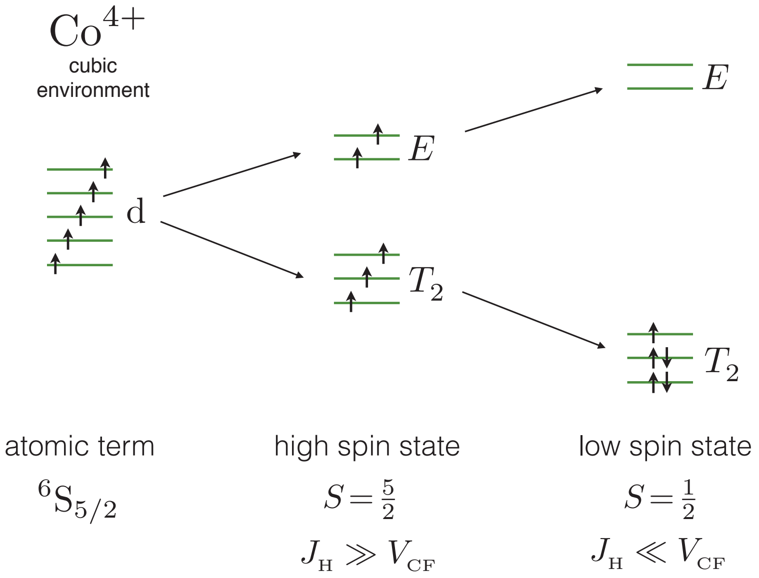

Figure 6.8: High spin and low spin states of the Co^{4+} ion in a cubic environment.

These may be each arranged into full terms by angular momentum addition to form $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, which yields $^2I = {}^2I_{13/2} \oplus {}^2I_{11/2}$, $^4F = {}^4F_{9/2} \oplus {}^4F_{7/2} \oplus {}^4F_{5/2} \oplus {}^4F_{3/2}$, *etc.*[11] The high spin state came from the term $^6S_{5/2}$. The low spin states must then be linear combinations of the $^4D_{1/2}$, $^4P_{1/2}$, $^2P_{1/2}$, and $^2S_{1/2}$ terms. These latter states all transform according to the Δ_6 IRREP of O', whereas $^6S_{5/2} = \Delta_7 \oplus \Delta_8$. Therefore, there must be a level crossing as V_{CF} is increased and we transition from high spin state to low spin state.

The oxides of Mn, Fe, Cu, and Co are quite rich in their crystal chemistry, as these ions may exist in several possible oxidation states (*e.g.* Co^{2+}, Co^{3+}, Co^{4+}) as well as various coordinations such as tetrahedral, pyramidal, cubic/octahedral. The cobalt oxides are particularly so because Co may exist in high spin, low spin, and even intermediate spin states. Co^{2+} is always in the high spin state $T_2^5\,E^2$ ($S = \frac{3}{2}$), while Co^{4+}, which we have just discussed, is usually in the low spin state $T_2^5\,E^0$ ($S = \frac{1}{2}$). Co^{3+} exists in three possible spin states: high ($T_2^4\,E^2$, $S = 2$), intermediate ($T_2^5\,E^1$, $S = 1$), and low ($T_2^6\,E^0$, $S = 0$). Such a complex phenomenology derives from the sensitivity of V_{CF} to changes in the Co-O bond length and Co-O-Co bond angle[12].

---

[11] The full decomposition of the [Ar] $4s^0\,4d^5$ configuration into terms is then

$$\begin{aligned}[\mathrm{Ar}]\,4s^0\,4d^5 = {} & {}^2I_{13/2} \oplus {}^2I_{11/2} \oplus {}^2H_{11/2} \oplus {}^2H_{9/2} \oplus {}^4G_{11/2} \oplus {}^4G_{9/2} \oplus {}^4G_{7/2} \oplus {}^4G_{5/2} \oplus 2 \cdot {}^2G_{9/2} \oplus 2 \cdot {}^2G_{7/2} \oplus {}^4F_{9/2} \\ & \oplus {}^4F_{7/2} \oplus {}^4F_{5/2} \oplus {}^4F_{3/2} \oplus 2 \cdot {}^2F_{7/2} \oplus 2 \cdot {}^2F_{5/2} \oplus {}^4D_{7/2} \oplus {}^4D_{5/2} \oplus {}^4D_{3/2} \oplus {}^4D_{1/2} \oplus 3 \cdot {}^2D_{5/2} \\ & \oplus 3 \cdot {}^2D_{3/2} \oplus {}^4P_{5/2} \oplus {}^4P_{3/2} \oplus {}^4P_{1/2} \oplus {}^2P_{3/2} \oplus {}^2P_{1/2} \oplus {}^6S_{5/2} \oplus {}^2S_{1/2} \quad .\end{aligned}$$

[12] See B. Raveau and M. M. Seikh, *Cobalt Oxides: From Crystal Chemistry to Physics* (Wiley, 2012).

C_3	E	C_3	C_3^2	
A	1	1	1	
E	1	ω	ω^2	
E^*	1	ω^2	ω	
$\boldsymbol{P}\,(1^-)$	3	0	0	$A \oplus E \oplus E^*$
$\boldsymbol{M}\,(1^+)$	3	0	0	$A \oplus E \oplus E^*$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	1	0	
$\boldsymbol{P}\,(1^-)$	3	0	1	$A_1 \oplus E$
$\boldsymbol{M}\,(1^+)$	3	0	-1	$A_2 \oplus E$

Table 6.11: Character tables for C_3 and C_{3v} and decomposition of $\boldsymbol{P}$ and $\boldsymbol{M}$. Here $\omega = e^{2\pi i/3}$.

6.3 Macroscopic Symmetry

Macroscopic properties of crystals[13] are described by *tensors*. The general formulation is

$$\theta_{a_1 \cdots a_k} = T^{j_1 \cdots j_n}_{a_1 \cdots a_k} \, h_{j_1 \cdots j_n} \quad . \tag{6.39}$$

where $\theta_{a_1 \cdots a_k}$ is an observable, $h_{j_1 \cdots j_n}$ is an applied field, and $T^{j_1 \cdots j_n}_{a_1 \cdots a_k}$ is a *generalized susceptibility tensor*. The *rank* of a tensor is the number of indices it carries. Examples include dielectric response, which is a second rank tensor:

$$D_\mu(\boldsymbol{k},\omega) = \varepsilon_{\mu\nu}(\boldsymbol{k},\boldsymbol{\omega}) \, E_\nu(\boldsymbol{k},\omega) \quad . \tag{6.40}$$

Nonlinear response such as second harmonic generation is characterized by a rank three tensor,

$$D^{(2)}_\mu(2\omega) = \chi_{\mu\nu\lambda}(2\omega,\omega,\omega) \, E_\nu(\omega) \, E_\lambda(\omega) \quad . \tag{6.41}$$

Another example comes from the theory of elasticity, where the *stress tensor* $\sigma_{\alpha\beta}(\boldsymbol{r})$ is linearly related to the local *strain tensor* $\varepsilon_{\mu\nu}(\boldsymbol{r})$ by a fourth rank *elastic modulus tensor* $C_{\alpha\beta\mu\nu}$,

$$\sigma_{\alpha\beta}(\boldsymbol{r}) = C_{\alpha\beta\mu\nu} \, \varepsilon_{\mu\nu}(\boldsymbol{r}) \quad . \tag{6.42}$$

We shall discuss the elastic modulus tensor in greater detail further below.

These various tensors must be invariant under all point group operations, a statement known as *Neumann's principle*. Note that this requires that the symmetry group $\mathcal{G}$ of a given tensor T must contain the crystallographic point group, *i.e.* $\mathcal{P} \subset \mathcal{G}$, but does not preclude the possibility that $\mathcal{G}$ may contain additional symmetries. One might ask what happens in nonsymmorphic crystals, when the space group is generated by translations and by elements $\{\, g \,|\, \boldsymbol{\tau}_g \,\}$ with $\boldsymbol{\tau}_g \neq 0$. The answer is that macroscopic properties of crystals cannot depend on these small translations within each unit cell.

6.3.1 Ferroelectrics and ferromagnets

A crystal may also exhibit a permanent electric ($\boldsymbol{P}$) or magnetic ($\boldsymbol{M}$) polarization. Any such vector must be invariant under all point group operations, *i.e.* $\boldsymbol{P} = \hat{g}\boldsymbol{P} \;\forall\; g \in \mathcal{P}$, with the same holding for $\boldsymbol{M}$[14]. In

---

[13] See C. S. Smith, *Solid State Physics* **6**, 175 (1958) for a review.

[14] We write $\hat{g}\boldsymbol{P}$ for the action of the group operation g on the quantity $\boldsymbol{P}$.

$\boldsymbol{P}\,(1^-)$	C_1	C_2	C_3	C_4	C_6	C_s	C_{2v}	C_{3v}	C_{4v}	C_{6v}
	1	2	3	4	6	m	$mm2$	$3m$	$4mm$	$6mm$
$\boldsymbol{M}\,(1^+)$	C_1	C_2	C_3	C_4	C_6	C_i	C_{2h}	S_6	C_{4h}	C_{6h}
	1	2	3	4	6	$\overline{1}$	$2/m$	$\overline{3}$	$4/m$	$6/m$

Table 6.12: Point groups supporting ferroelectricity and ferromagnetism.

component notation, we have

$$(\hat{g}\boldsymbol{P})_\nu = P_\mu\, D_{\mu\nu}(g) \quad , \tag{6.43}$$

where $D_{\alpha\beta}(g)$ is the matrix representation of g. Clearly any point group $\mathcal{P}$ which contains the inversion element I does not allow for a finite polarization, since $D_{\mu\nu}(I) = -\delta_{\mu\nu}$.

If Ψ is the (generally reducible) representation under which $\boldsymbol{P}$ or $\boldsymbol{M}$ or indeed any susceptibility tensor $X^{j_1\cdots j_n}_{a_1\cdots a_k}$ transforms, then the number of real degrees of freedom associated with the tensor is the number of times it contains the trivial IRREP of $\mathcal{P}$, *i.e.* the number of degrees of freedom is

$$n(\Psi) = \frac{1}{N_G} \sum_{\mathcal{C}} N_{\mathcal{C}}\, \chi^\Psi(\mathcal{C}) \quad . \tag{6.44}$$

Recall that $\chi(\mathcal{C}) = 1$ for all classes in the trivial representation. Examining the character tables for C_3 and C_{3v}, we see that $n(1^\pm) = 1$ in C_3, but in C_{3v} we have $n(1^-) = 1$ but $n(1^+) = 0$. We conclude that any crystal with a nonzero magnetization density $\boldsymbol{M} \neq 0$ cannot be one of C_{3v} symmetry. In general, the condition for a point group to support ferroelectricity is that it be *polar*, *i.e.* that it preserve an axis, which is the axis along which $\boldsymbol{P}$ lies. Of the 32 crystallographic point groups, ten are polar. The cyclic groups C_n support ferromagnetism, and since 1^+ is even under inversion, adding I to these groups is also consistent with finite $\boldsymbol{M}$. For all point groups other than those listed in Tab. 6.12, we have $n(1^\pm) = 0$. For example, in D_{3d}, we found $1^\pm = A_{2\pm} \oplus E_\pm$ (see Tab. 6.8). In O_h, we found $1^\pm = T_{1\pm}$ (see Tab. 6.5 and add $\pm = g/u$ when inversion is present). In neither case is the trivial representation present in the decomposition. Note that $C_s \cong C_{1v}$.

If we orient the symmetry axis of these groups along $\hat{\boldsymbol{z}}$, we find, upon using the character tables and the decomposition formula in Eqn. 6.44,

$$\boldsymbol{P}(C_1) = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} \quad , \quad \boldsymbol{P}(C_s) = \begin{pmatrix} P_x \\ P_y \\ 0 \end{pmatrix} \quad , \quad \boldsymbol{P}(C_{n>2}\,,\, C_{n>2\,v}) = \begin{pmatrix} 0 \\ 0 \\ P_z \end{pmatrix} \tag{6.45}$$

and

$$\boldsymbol{M}(C_1) = \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} \quad , \quad \boldsymbol{M}(C_i) = \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} \quad , \quad \boldsymbol{M}(C_{n>2}\,,\, C_{n>2} \times C_i) = \begin{pmatrix} 0 \\ 0 \\ M_z \end{pmatrix} \quad , \tag{6.46}$$

with $\boldsymbol{P} = \boldsymbol{M} = 0$ in the case of all other groups.

6.3.2 Spontaneous symmetry breaking

Homage to Socrates, Galileo, Coleman, and Zee:

> *Sagredo* : This thing you have demanded, *i.e.* that $\hat{g}\boldsymbol{M} = \boldsymbol{M}$ for all point group operations $g \in \mathcal{P}$, I fear is asking too much. For I learned in Professor McX's class about the wondrous phenomenon of *spontaneous symmetry breaking*, the whole point of which is that as a parameter is varied, if our crystal be in the thermodynamic limit, the symmetry of the ground state may indeed become lower than that of the Hamiltonian itself. Should not we then expect $\hat{g}\boldsymbol{M} \neq \boldsymbol{M}$ when g corresponds to the action of one of the so-called *broken generators* of the symmetry group?
>
> *Salviati* : Thou hast learnt well, and McX ought be well pleased by your understanding. But thy question contains the seeds of its own answer. For surely the symmetry group of the Hamiltonian, that which describes all the particles in a crystal, is indeed that most sublime and continuous group $\mathsf{O}(3)$, appended, if need be, by the $\mathsf{SU}(2)$ of spin. The very fact that a crystal hath a point group $\mathcal{P}$ with symmetry lower than that of $\mathsf{O}(3)$ heralds the spontaneous symmetry breaking which resulted in that crystalline phase in the first place. When we demand $\hat{g}\boldsymbol{M} = \boldsymbol{M}$ for all $g \in \mathcal{P}$, we are saying that a spontaneous moment $\boldsymbol{M}$ is consistent only with certain point groups.
>
> *Sagredo* : Master, thou didst remove the scales from before my eyes, that I might see what the gods have ordained! For if a spontaneous moment $\boldsymbol{P}$ or $\boldsymbol{M}$ were to develop felicitously in a crystal, it would, through electroelastic or magnetoelastic couplings, by necessity induce some small motions of the ions. Thus, any transition where a spontaneous polarization or magnetization ensues must be concomitant with a *structural deformation* if the high symmetry phase doth not permit a finite $\boldsymbol{P}$ or $\boldsymbol{M}$.
>
> *Salviati* : Indeed it is so. Your words are excellent.
>
> *Sagredo* : And therefore, a material of the cubic affiliation, such as iron, whose point group abhoreth a spontaneous magnetization, is held accurs'd, for it could never become a ferromagnet…
>
> *Salviati* : Well, um…you see…
>
> *Simplicio* : I'm hungry. Let's get sushi.

Simplicio has pulled Salviati's chestnuts out of the fire with his timely suggestion, but to Sagredo's last point, it is generally understood that a tetragonal deformation in α-Fe must accompany its ferromagnetic transition at $T_{\mathrm{C}} = 1043\,\mathrm{K}$. However, the resulting value of $(c-a)/a$ is believed to be on the order of 10^{-6}, based on magnetostriction measurements[15], which is to say a shift in the c-axis length by a distance smaller than a nuclear diameter. So far as I understand, the putative tetragonal distortion is too weak to be observed at present[16].

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[15] See E. du Tremolet *et al.*, *J. Mag. Magn. Mat.* **31**, 837 (1983).

[16] In fact, since D_{4h} does not accommodate a nonzero $\boldsymbol{M}$, the ferromagnetic phase of α-Fe must have C_{4h} symmetry, which is not a holohedral point group. *I.e.* α-Fe below T_{C} is either not a Bravais lattice, or its crystallographic symmetry is further broken down to monoclinic, *i.e.* C_{2h}.

6.3.3 Pyroelectrics, thermoelectrics, ferroelectrics, and piezoelectrics

Let's just get all this straight right now, people:

- *Pyroelectric* : A pyroelectric material possesses a spontaneous polarization $\boldsymbol{P}$ below a critical temperature $T_{\rm c}$. This is due to the formation of a dipole moment $\boldsymbol{p}$ within each unit cell of the crystal. The Greek root *pyr-* means "fire", and the pyroelectric coefficient is defined to be $\boldsymbol{\gamma} = d\boldsymbol{P}/dT$. In the presence of an external electric field $\boldsymbol{E}$, one has $\boldsymbol{P} = \boldsymbol{P}_{\rm ind} + \boldsymbol{P}_{\rm s}$, where $\boldsymbol{P}_{\rm ind} = \chi \boldsymbol{E}$ is the *induced polarization*, with χ the polarization tensor, and $\boldsymbol{P}_{\rm s}$ is the *spontaneous polarization*. One then has $\boldsymbol{\gamma} = d\boldsymbol{P}_{\rm s}/dT$. We regard $\boldsymbol{\gamma}$ as a rank one tensor, since T is a scalar. Pyroelectric crystals were known to the ancient Greeks, and in the $18^{\rm th}$ century it was noted that tourmaline crystals develop charges at their faces upon heating or cooling.

- *Thermoelectric* : The thermoelectric effect is the generation of an electric field due in a sample with a fixed temperature *gradient*. One has $\boldsymbol{\mathcal{E}} = \rho \boldsymbol{j} + Q \boldsymbol{\nabla} T$, where $\boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}(\phi - e^{-1}\mu)$ is the gradient of the electrochemical potential and $\boldsymbol{j}$ is the electrical current. The response tensors ρ and Q are the electrical resistivity and the *thermopower* (also called the *Seebeck coefficient*), respectively. The units of thermopower are $k_{\rm B}/e$, and Q has the interpretation of the entropy carried per charge.

  Note that despite the similarity in their names (*thermo-* is the Greek root for "heat"), thermoelectricity and pyroelectricity are distinct phenomena. In a pyroelectric, the change in temperature ΔT is uniform throughout the sample. A change in temperature will result in a change of the dipole moment per cell, and the accumulation of surface charges and a potential difference which gradually decays due to leakage. Almost every material, whether a metal or an insulator, whether or not a polar crystal, will exhibit a thermoelectric effect[17]. The electric field will remain so long as the temperature gradient $\boldsymbol{\nabla} T$ is maintained across the sample.

- *Ferroelectric* : For our purposes, there is no distinction between a ferroelectric and a pyroelectric. However, in the literature, the distinction lies in the behavior of each in an external electric field $\boldsymbol{E}$. The spontaneous polarization $\boldsymbol{P}_{\rm s}$ of a ferroelectric can be reversed by the application of a sufficiently strong $\boldsymbol{E}$ field. In a pyroelectric, this coercive field exceeds the breakdown field, so the dipole reversal cannot be accomplished. In a ferroelectric, the dipole moment can be reversed.

- *Piezoelectric* : Piezoelectricity occurs in 20 of the 21 noncentrosymmetric crystallographic point groups, the exception being the cubic group O (432). The polarization of a piezoelectric is changed by applying stress: $\Delta P_\mu = d_{\mu\nu\lambda}\, \sigma_{\nu\lambda}$, where $\Delta \boldsymbol{P} = \boldsymbol{P} - \boldsymbol{P}_{\rm s}$ and $\sigma_{\nu\lambda}$ is the stress tensor. We shall discuss the piezoelectric tensor $d_{\mu\nu\lambda}$ more below. The hierarchy of these phenomena is then

  $$\text{ferroelectric} \subset \text{pyroelectric} \subset \text{piezoelectric} \quad ,$$

  with thermoelectricity being unrelated to the other three.

  The Ginzburg-Landau free energy for an isotropic pyroelectrics or ferroelectrics is modeled by

  $$f(P,E) = f_0 + aP^2 + bP^4 + cP^6 - EP \quad , \tag{6.47}$$

---

[17] The exception is the case of superconductors, which have zero Seebeck coefficient because the Cooper pairs carry zero entropy.

where $E = \boldsymbol{E}\cdot\hat{\boldsymbol{n}}$ is the projection of the external electric field along the invariant axis of the pyroelectric's point group, $a \propto T - T_{\rm c}$, and $c > 0$. If $b > 0$ the transition at $T = T_{\rm c}$ is second order, while if $b < 0$ the second order transition is preempted by a first order one at $a = \frac{3}{16}(b^2/c)$. But what do we mean by P in eqn. 6.47? If the high symmetry (*i.e.* $\boldsymbol{P} = 0$ when $\boldsymbol{E} = 0$) crystalline phase is of cubic symmetry, we should write

$$\begin{aligned} f(\boldsymbol{P},\boldsymbol{E}) = f_0 &+ a(P_x^2 + P_y^2 + P_z^2) + b_1(P_x^4 + P_y^4 + P_z^4) + b_2(P_x^2P_y^2 + P_y^2P_z^2 + P_x^2P_z^2) \\ &+ c_1(P_x^6 + P_y^6 + P_z^6) + c_2(P_x^4P_y^2 + P_x^4P_z^2 + P_y^4P_x^2 + P_y^4P_z^2 + P_z^4P_x^2 + P_z^4P_y^2) \\ &+ c_3P_x^2P_y^2P_z^2 - \boldsymbol{E}\cdot\boldsymbol{P} + \mathcal{O}(\boldsymbol{P}^8) \quad . \end{aligned} \tag{6.48}$$

Ferroelectricity in barium titanate

A parade example of ferroelectricity is barium titanate depicted in Fig. 6.9. $BaTiO_3$ has four structural phases:

(i) a high temperature cubic phase (C) for $T \gtrsim 393\,{\rm K}$

(ii) an intermediate temperature tetragonal phase (T) for $T \in [\sim 282\,{\rm K}\,,\, \sim 393\,{\rm K}]$

(iii) a second intermediate temperature orthorhombic phase (O) for $T \in [\sim 183\,{\rm K}\,,\, \sim 282\,{\rm K}]$

(iv) a low temperature rhombohedral (trigonal) phase (R) for $T \lesssim 183\,{\rm K}$.

All but the high temperature cubic phase exhibit ferroelectricity, *i.e.* spontaneous polarization which may be reversed by the application of an external electric field. These phases have traditionally been

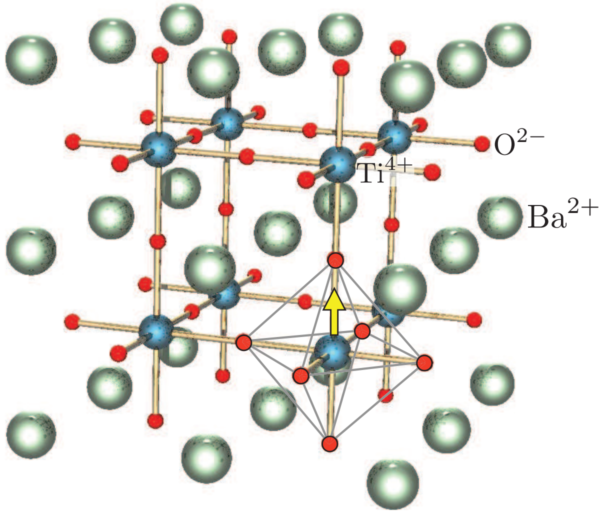

Figure 6.9: High temperature cubic perovskite crystal structure of $BaTiO_3$. Ba^{2+} sites are in green, Ti^{4+} in blue, and O^{2-} in red. The yellow arrow shows the direction in which the Ti^{4+} ion moves as the material is cooled below $T_{\rm c}$ within the displacive model. Image credit: Wikipedia.

understood in terms of the displacement of the Ti^{4+} ion within each unit cell. In the cubic phase, each Ti^{4+} ion sits in the center of an oxygen octahedron, and the free energy density from eqn. 6.48 is $f_{\text{C}} = f_0$. The three ordered phases have $\boldsymbol{P} = P\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}_{\text{C}} = (0,0,1)$, $\hat{\boldsymbol{n}}_{\text{O}} = \frac{1}{\sqrt{2}}(0,1,1)$, and $\hat{\boldsymbol{n}}_{\text{R}} = \frac{1}{\sqrt{3}}(1,1,1)$. Each of these phases is described by a sixth order Landau free energy of the form of eqn. 6.47, with

$$b_{\text{T}} = b_1 \quad , \quad b_{\text{O}} = \tfrac{1}{2}b_1 + \tfrac{1}{4}b_2 \quad , \quad b_{\text{R}} = \tfrac{1}{3}b_1 + \tfrac{1}{3}b_2 \tag{6.49}$$

and

$$c_{\text{T}} = c_1 \quad , \quad c_{\text{O}} = \tfrac{1}{2}c_1 + \tfrac{1}{2}c_2 \quad , \quad c_{\text{R}} = \tfrac{1}{9}c_1 + \tfrac{2}{9}c_2 + \tfrac{1}{27}c_3 \quad . \tag{6.50}$$

Minimizing the free energy in phase $j \in \{\text{T},\text{O},\text{R}\}$ yields the equation $a + 2b_j P_j^2 + 3c_j P_j^4 = 0$, with solution

$$P_j(T) = \frac{-b_j + \sqrt{b_j^2 - 3ac_j}}{3c_j} \quad , \tag{6.51}$$

where $a = \alpha(T - T_{\text{c}})$ and $T_{\text{c}} \approx 393\,\text{K}$. The free energy in phase j is then obtained by substituting the result for $P = P_j$ into $f_j(T) = f_0 + a_j P^2 + b_j P^4 + c_j P^6$.

Provided $b_{\text{T}} > b_{\text{O}}$ and b_{R}, the second order transition at $a = 0$ (*i.e.* $T = T_{\text{c}}$) is from cubic to tetragonal. As one lowers the temperature further, one encounters two first order transitions, first from tetragonal to orthorhombic, and second from orthorhombic to rhombohedral (trigonal)[18]. These transitions occur at temperatures where $f_{\text{T}}(T'_{\text{c}}) = f_{\text{O}}(T'_{\text{c}})$ and $f_{\text{O}}(T''_{\text{c}}) = f_{\text{R}}(T''_{\text{c}})$.

The standard displacive model of ferroelectricity in BaTiO_3 is unable to explain several experiments, however. In the displacive model the high temperature cubic phase has point group O_h. This would mean that first order Raman scattering is forbidden, because, as we shall see below in §6.4.3, Raman scattering preserves parity, and thus the low energy, odd parity long wavelength phonons are all Raman inactive. Yet a healthy first order Raman signal is observed[19]. A second problem is that one expects on general grounds soft modes with frequencies tending toward zero as one approaches a second order phase transition. Yet experiments show damped but finite frequency modes at the cubic to tetragonal transition[20]. Finally, aspects of the observed x-ray scattering are difficult to understand within the displacive model. In particular , x-ray fine structure measurements show in all phases that the Ti^{4+} ions are displaced along different $\langle 111 \rangle$ directions[21]. In 2006, Zhang, Cagin, and Goddard[22] (ZCG) presented results from a density functional calculation the results of which differed from those of the displacive model. Rather than an undistorted cubic phase, ZCG found that the C phase is *antiferroelectric*, with a $2 \times 2 \times 2$ unit cell (see Fig. 6.10). In the T and O phases, there is mixed ferroelectric and antiferroelectric order, and only in the R phase is the material purely ferroelectric. The associated space and point group symmetries are listed in tab. 6.13.

Note that while C_{4v} is a subgroup of O_h, it is not a subgroup of T_d. Thus, the C to T transition is predicted to be first order according to ZCG. Their identification of the symmetries of the various phases also resolves the aforementioned difficulties in reconciling the displacive model with experimental data.

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[18] Within Landau theory, the order of the transitions will depend on details of the Landau parameters.

[19] A. M. Quittet and M. Lambert, *Solid State Comm.* **12**, 1053 (1973).

[20] Y. Luspin, J. L. Servoin, and F. Gervais, *J. Phys. C Solid State* **13**, 3761 (1980).

[21] B. Ravel *et al.*, *Ferroelectrics* **206**, 407 (1998).

[22] Q. Zhang, T. Cagin, and W. A. Goddard III, *Proc. Natl. Acad. Sci.* **103**, 14695 (2006).

phase	displacive model		DFT results	
	$\mathcal{S}$	$\mathcal{P}$	$\mathcal{S}$	$\mathcal{P}$
cubic	$Pm\overline{3}m$	$m\overline{3}m = O_h$	$I\overline{4}3m$	$\overline{4}3m = T_d$
tetrahedral	$P4mm$	$4mm = C_{4v}$	$I4cm$	$4mm = C_{4v}$
orthorhombic	$Amm2$	$mm2 = C_{2v}$	$Pmn2_1$	$mm2 = C_{2v}$
rhombohedral	$R3m$	$3m = C_{3v}$	$R3m$	$3m = C_{3v}$

Table 6.13: Phases of $BaTiO_3$ and their space and point groups.

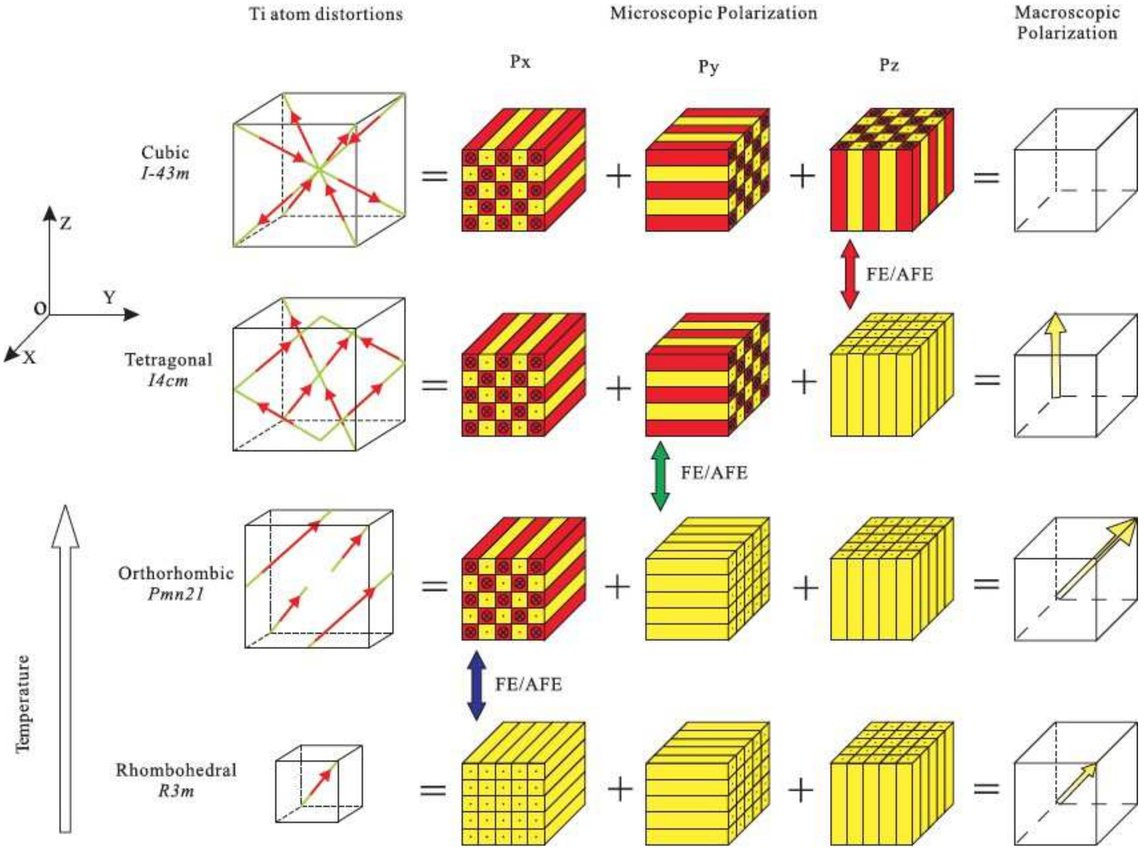

Figure 6.10: Fig. 1 from Zhang, Cagin, and Goddard (2006) showing Ti^{4+} ion distortions and polarizations in $BaTiO_3$, as determined from density functional calculations.

6.3.4 Second rank tensors : conductivity

The conductivity $\sigma_{\mu\nu}$ and dielectric susceptibility $\varepsilon_{\mu\nu}$ are examples of second rank tensors, *i.e.* matrices, which relate a vector cause ($\boldsymbol{E}$) to a vector effect ($\boldsymbol{j}$ or $\boldsymbol{D}$)[23]. The action of a group element g on a second rank tensor $T_{\mu\nu}$ is given by

$$(\hat{g}\, T)_{\alpha\beta} = T_{\mu\nu}\, D_{\mu\alpha}(g)\, D_{\nu\beta}(g) \quad . \tag{6.52}$$

Thus the tensor $T_{\mu\nu}$ transforms according to the product representation $\varPsi(G) = D(G) \times D(G)$. Recall that product representations were discussed earlier in §2.4.7 and §3.2.

The product representation can be reduced to the symmetric (S) and antisymmetric (A) representations, which themselves may be further reduced within a given symmetry group G. Recall the characters in these representations are given by (see §3.2.2)

$$\chi^{\mathsf{S,A}}(g) = \tfrac{1}{2}\big[\chi(g)\big]^2 \pm \tfrac{1}{2}\,\chi(g^2) \quad . \tag{6.53}$$

Note that any equilibrium thermodynamic response function $T_{\mu\nu} = -\partial^2 F/\partial h_\mu\, \partial h_\nu$, where $\boldsymbol{h}$ is an applied field, will necessarily transform according to the symmetric product representation $\varPsi^{\mathsf{S}}$. The number of independent components of a general response tensor will then be given by

$$n(\varPsi^{\mathsf{S,A}}) = \frac{1}{N_G} \sum_{\mathcal{C}} N_{\mathcal{C}}\, \chi^{\mathsf{S,A}}(\mathcal{C}) \quad . \tag{6.54}$$

Let's work this out for the group C_{3v}, the vector representation 1^- of which has characters $\chi(E) = 3$, $\chi(2C_3) = 0$, and $\chi(3\sigma_v) = 1$ (see Tab. 6.11). From these values, we obtain

$$\chi^{\mathsf{S}}(E) = 6 \quad , \quad \chi^{\mathsf{S}}(2C_3) = 0 \quad , \quad \chi^{\mathsf{S}}(3\sigma_v) = 2 \tag{6.55}$$

$$\chi^{\mathsf{A}}(E) = 3 \quad , \quad \chi^{\mathsf{A}}(2C_3) = 0 \quad , \quad \chi^{\mathsf{A}}(3\sigma_v) = -1 \quad , \tag{6.56}$$

and we then compute $n(\varPsi^{\mathsf{S}}) = 2$ and $n(\varPsi^{\mathsf{A}}) = 0$. The full decomposition into C_{3v} IRREPs is found to be $\varPsi^{\mathsf{S}} = 2A_1 \oplus 2E$ and $\varPsi^{\mathsf{A}} = A_2 \oplus E$. We conclude that the most general symmetric tensor invariant under C_{3v} is of the form $\mathsf{diag}(a, a, c)$, where $\hat{\boldsymbol{z}}$ is the symmetry axis. The antisymmetric component vanishes entirely, because $\varPsi^{\mathsf{A}} = 1^+$ does not contain the trivial A_1 IRREP. However, note that $n_{A_2}(\varPsi^{\mathsf{A}}) = 1$, which means that the tensor

$$T = \begin{pmatrix} a & d & 0 \\ -d & a & 0 \\ 0 & 0 & c \end{pmatrix} \tag{6.57}$$

is permissible with nonzero a, c, and d *if and only if a and c transform as A_1 and d transforms as A_2*. For example, the conductivity tensor may be of the form

$$\sigma = \begin{pmatrix} \sigma_\perp(H_z) & f(H_z) & 0 \\ -f(H_z) & \sigma_\perp(H_z) & 0 \\ 0 & 0 & \sigma_\parallel(H_z) \end{pmatrix} \quad , \tag{6.58}$$

where $f(H_z)$ is an odd function of the magnetic field component along the symmetry axis. The quantities $\sigma_{\perp,\parallel}(H_z)$ are constants invariant under all C_{3v} operations and are even functions of H_z.

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[23] Of course the dielectric and conductivity tensors are related by $\varepsilon_{\mu\nu}(\boldsymbol{k},\omega) = \delta_{\mu\nu} + (4\pi i/\omega)\,\sigma_{\mu\nu}(\boldsymbol{k},\omega)$.

	elements of $T_{\mu\nu} = T_{\nu\mu}$					
crystal system	11	22	33	23	31	12
triclinic	a	b	c	f	e	d
monoclinic	a	b	c	0	0	d
orthorhombic	a	b	c	0	0	0
trigonal	a	a	c	0	0	0
tetragonal	a	a	c	0	0	0
hexagonal	a	a	c	0	0	0
cubic	a	a	a	0	0	0

Table 6.14: Allowed nonzero entries of symmetric rank two tensors by crystal system. Crystallographic axes are assumed.

C_{3v} is a trigonal point group. For the others, the allowed nonzero elements of a symmetric tensor T are given in Tab. 6.14. Note that cubic symmetry requires that any symmetric rank two tensor be a multiple of the identity. This means, for example, that the inertia tensor $I_{\alpha\beta}$, with the origin at the center of a uniform cube, is a multiple of the identity[24], and thus independent of the cube's orientation. This entails, for example, that if a cube is used to construct a torsional pendulum, the frequency of the oscillations will be the same whether the torsional fiber runs through a face center, a corner, an edge center, or indeed any point on the cube's surface, so long as it also runs through the cube's center.

Representation ellipsoid

Given a dimensionless rank two tensor $T_{\mu\nu}$, one can form the function $T(\boldsymbol{r}) = T_{\mu\nu}\, x^{\mu}\, x^{\nu}$. The locus of points $\boldsymbol{r}$ for which $T(\boldsymbol{r}) = \pm 1$ is called the *representation ellipsoid* of $T_{\mu\nu}$. Clearly any antisymmetric part of T will be projected out in forming the function $T(\boldsymbol{r})$ and will not affect the shape of the representation ellipsoid. In fact, $T(\boldsymbol{r}) = \pm 1$ defines an ellipsoid only if all the eigenvalues of T are of the same sign. Else it defines a hyperboloid. For any real symmetric matrix, the eigenvalues are real and the eigenvectors are mutually orthogonal, or may be chosen to be so in the case of degeneracies.

For triclinic systems, the ellipsoid axes are under no restriction. For monoclinic systems, one of the ellipsoid's axes must be the twofold axis of the crystal. For orthorhombic systems, all three axes of the ellipsoid are parallel to the crystalline axes. For trigonal, tetragonal, and hexagonal crystals, two of the eigenvalues are degenerate (see Tab. 6.14), which means that the ellipsoid is a surface of revolution along the high symmetry axis of the crystal. *I.e.* the ellipsoid has an $\mathsf{O}(2)$ symmetry about this axis. Finally, for cubic systems, the representation ellipsoid is a sphere S^2.

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[24] $I_{\alpha\beta} = \frac{1}{6} M a^2\, \delta_{\alpha\beta}$ where M is the cube's mass and a its side length.

6.3.5 Third rank tensors : piezoelectricity

A common example of a third rank tensor comes from the theory of the piezoelectric effect. An applied stress $\sigma_{\nu\lambda}$ leads to a polarization density P_μ, where

$$P_\mu = d_{\mu\nu\lambda}\,\sigma_{\nu\lambda} \quad , \tag{6.59}$$

where $d_{\mu\nu\lambda}$ is the piezoelectric tensor. We can immediately say that if the point group $\mathcal{P}$ contains the inversion element I, then $d_{\mu\nu\lambda} = 0$, because $D_{\mu\mu'}(I) = -\delta_{\mu\mu'}$ and therefore $\hat{I}\,d_{\mu\nu\lambda} = -d_{\mu\nu\lambda}$.

Since the stress tensor σ is symmetric (see below), it contains six independent elements, the piezoelectric tensor $d_{\mu\nu\lambda}$ is itself symmetric in its last two indices[25], *i.e.* $d_{\mu\nu\lambda} = d_{\mu\lambda\nu}$. Accordingly one may define the composite index $(\nu\lambda) \to a$, as defined in the following table:

$(\nu\lambda)$:	(11)	(22)	(33)	(23)	(31)	(12)
a :	1	2	3	4	5	6

Table 6.15: Composite indices for symmetric rank two tensors.

If we then define $d_{\mu 4} \equiv d_{\mu 23} = d_{\mu 32}$, $d_{\mu 5} \equiv d_{\mu 31} = d_{\mu 13}$, and $d_{\mu 6} \equiv d_{\mu 12} = d_{\mu 21}$, we may represent the tensor multiplication in Eqn. 6.59 as an ordinary matrix multiplication, *viz.*

$$\begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ 2\sigma_4 \\ 2\sigma_5 \\ 2\sigma_6 \end{pmatrix} \quad , \qquad \sigma = \begin{pmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{pmatrix} \quad . \tag{6.60}$$

Note the appearance of a factor of two in the last three elements of the column vector of stresses.

Now let's consider how the symmetry under a point group $\mathcal{P}$ restricts the form of $d_{\mu a}$.

- For triclinic crystals with point group C_1, there is no restriction, and $d_{\mu a}$ contains 18 independent elements. If $\mathcal{P} = C_i$, which contains inversion, then of course $d_{\mu a} = 0$ for all (μ, a).
- For monoclinic crystals, the highest symmetry without inversion is C_s, which is generated by the identity and reflections $z \to -z$. All piezoelectric tensor elements $d_{\mu\nu\lambda}$ in which the index $3(z)$ appears an odd number of times must vanish. For the rectangular 3×6 matrix $d_{\mu a}$, this means that the following eight elements vanish by symmetry:

  $$d_{14} = d_{15} = d_{24} = d_{25} = d_{31} = d_{32} = d_{33} = d_{36} = 0 \quad . \tag{6.61}$$

  We are left with ten independent piezoelectric constants for the group C_s, which is also a polar point group, and hence can support ferroelectricity or ferromagnetism. The general form of the

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[25] Thus $d_{\mu\nu\lambda}$ is not the most general rank three tensor possible.

3×6 piezoelectric tensor is

$$d^{\mathsf{MONO}}_{\mu a}[C_s] = \begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{pmatrix} \quad . \tag{6.62}$$

- For orthorhombic crystals, the only point groups without inversion C_{2v} and D_2. Consider first C_{2v}, in which $x \to -x$ and $y \to -y$ are symmetries, though not $z \to -z$[26]. The only nonzero piezoelectric tensor elements are those with an even number of indices of 1(x) and 2(y), which means that only five elements of $d_{\mu a}$ may be nonzero, and the general form for $d_{\mu a}$ within C_{2v} is

  $$d^{\mathsf{ORTHO}}_{\mu a}[C_{2v}] = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.63}$$

  Note that C_{2v} is polar. For D_2, which is nonpolar, the only nonzero elements are d_{14} , d_{25} , and d_{36} .

- For tetragonal crystals, the highest symmetries not containing inversion are D_{2d} , C_{4v} , D_4 , and C_{4h}. Consider the case D_{2d}. Any point (x, y, z) has symmetry-related images at $(-x, -y, z)$, (y, x, z), and $(x, -y, -z)$, which allows only for two independent nonzero piezoelectric tensor elements: $d_{14} = d_{25}$ and d_{36} . The group D_{2d} is nonpolar. For D_4, there is only one independent nonzero element: $d_{14} = -d_{25}$. The lowest point group symmetry in the tetragonal system is C_4, which relates (x, y, z) to $(-y, x, z)$. This allows for the four independent nonzero piezoelectric tensor elements:

  $$d^{\mathsf{TET}}_{\mu a}[C_4] = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.64}$$

  Reducing the symmetry to C_{4v} eliminates d_{14}, and there are only three independent moduli. For S_4, relative to C_4, we have $d_{32} = -d_{31}$, we lose d_{33} but gain d_{36}, so again there are four independent moduli.

- For trigonal crystals, the highest symmetry noncentrosymmetric point group is D_3 The implementation of the symmetry restrictions here is a little bit more involved because of the threefold rotations and is left as an exercise to the student. There are three independent piezoelectric coefficients:

  $$d^{\mathsf{TRIG}}_{\mu a}[D_3] = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.65}$$

  The lowest within the trigonal class is C_3, for which there are six independent moduli:

  $$d^{\mathsf{TRIG}}_{\mu a}[C_3] = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.66}$$

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[26] If we would include a third orthogonal reflection, we'd then have inversion, in which case all $d_{\mu\nu\lambda} = 0$.

Increasing the symmetry to C_{3v}, we lose d_{14} and d_{26}, so there are four independent moduli:

$$d^{\mathsf{TRIG}}_{\mu a}[C_{3v}] = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.67}$$

Both C_{3v} and C_3 are polar.

- For hexagonal crystals, we begin with the lowest symmetry group in the system, C_6. There are four independent elastic moduli, with

$$d^{\mathsf{HEX}}_{\mu a}[C_6] = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.68}$$

Increasing the symmetry to C_{6v}, one loses a modulus, with $d_{14} = 0$. Starting with C_{3h} , one has two independent moduli:

$$d^{\mathsf{HEX}}_{\mu a}[C_{3h}] = \begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad . \tag{6.69}$$

Increasing the symmetry to D_{3h}, we lose d_{11} due to the twofold axis which sends (x, y, z) to $(-x, y, -z)$, and the only nonzero elements are $d_{16} = 2d_{21} = -2d_{22}$. Finally, for D_6, the only nonzero elements are $d_{14} = -d_{25}$.

- Finally we arrive at the cubic system. The centrosymmetric cubic point groups O_h and T_h of course do not support piezoelectricity. Surprisingly, while O is noncentrosymmetric, its symmetries are sufficient to disallow piezoelectricity as well, and $d_{\mu a} = 0$ for all elements. Thus, O is the sole example among the 21 noncentrosymmetric crystallographic point groups which does not allow for piezoelectric behavior. The point groups T and T_d support piezoelectricity, with one independent constant $d_{14} = d_{25} = d_{36}$. Neither is polar.

6.3.6 Fourth rank tensors : elasticity

Another example comes from the theory of elasticity, where an elastic medium is described by a local deformation field $\boldsymbol{u}(\boldsymbol{r})$, corresponding to the elastic displacement of the solid at $\boldsymbol{r}$. The *strain tensor* is defined by the dimensionless expression

$$\varepsilon_{ij}(\boldsymbol{r}) = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \quad . \tag{6.70}$$

Note that $\varepsilon = \varepsilon^{\mathsf{T}}$ is a symmetric tensor by definition. Similarly, the *stress tensor* $\sigma_{ij}(\boldsymbol{r})$ is defined by

$$dF_i(\boldsymbol{r}) = -\sigma_{ij}(\boldsymbol{r})\, n_j \, d\Sigma \quad , \tag{6.71}$$

where $d\boldsymbol{F}(\boldsymbol{r})$ is the differential force on a surface element $d\Sigma$ whose normal is the vector $\hat{\boldsymbol{n}}$. Angular momentum conservation requires that the stress tensor also be symmetric[27]. The stress and strain tensors are related by the rank four *elastic modulus tensor*, *viz.*

$$\sigma_{ij}(\boldsymbol{r}) = C_{ijkl}\,\varepsilon_{kl}(\boldsymbol{r}) = \frac{\delta f}{\delta\varepsilon_{ij}(\boldsymbol{r})} \quad , \tag{6.72}$$

where the second equality is a statement of thermal equilibrium akin to $p = -\partial F/\partial V$. Here,

$$f(\boldsymbol{r}) = f_0 + \tfrac{1}{2}\,C_{ijkl}\,\varepsilon_{ij}(\boldsymbol{r})\,\varepsilon_{kl}(\boldsymbol{r}) + \mathcal{O}(\varepsilon^3) \tag{6.73}$$

is the local free energy density. Since ε is a dimensionless tensor, the elastic moduli have dimensions of energy density, typically expressed in cgs units as $\mathrm{dyn/cm^2}$. For an *isotropic* material, the only $\mathsf{O}(3)$ invariant terms in the free energy to order ε^2 are proportional to either $(\mathsf{Tr}\,\varepsilon)^2$ or to $\mathsf{Tr}(\varepsilon^2)$. Thus,

$$f = f_0 + \tfrac{1}{2}\,\lambda\,(\mathsf{Tr}\,\varepsilon)^2 + \mu\,\mathsf{Tr}\,(\varepsilon^2) \quad . \tag{6.74}$$

The parameters λ and μ are called the *Lamé coefficients*[28]. For isotropic elastic materials, then,

$$\sigma_{ij} = \frac{\partial f}{\partial\varepsilon_{ij}} = \lambda\,\mathsf{Tr}\,\varepsilon\;\delta_{ij} + 2\mu\,\varepsilon_{ij} \quad . \tag{6.75}$$

In the literature, one often meets up with the quantity $K \equiv \lambda + \frac{2}{3}\mu$, in which case the free energy density becomes

$$f = f_0 + \tfrac{1}{2}K\,(\mathsf{Tr}\,\varepsilon)^2 + \mu\,\mathsf{Tr}\big(\varepsilon - \tfrac{1}{3}\,\mathsf{Tr}\,\varepsilon\big)^2 \tag{6.76}$$

The reason is that the tensor $\widetilde{\varepsilon} \equiv \varepsilon - \frac{1}{3}(\mathsf{Tr}\,\varepsilon)\cdot\mathbb{1}$ is traceless, and therefore the constant K tells us about *bulk deformations* while μ tells us about *shear deformations*. One then requires $K > 0$ and $\mu > 0$ for thermodynamic stability. We then may write, for isotropic materials,

$$\begin{aligned} \sigma &= K\,(\mathsf{Tr}\,\varepsilon)\cdot\mathbb{1} + 2\mu\,\widetilde{\varepsilon} \\ \varepsilon &= \frac{1}{9K}\,(\mathsf{Tr}\,\sigma)\cdot\mathbb{1} + \frac{1}{2\mu}\,\widetilde{\sigma} \quad , \end{aligned} \tag{6.77}$$

with $\widetilde{\sigma} \equiv \sigma - \frac{1}{3}(\mathsf{Tr}\,\sigma)\cdot\mathbb{1}$ the traceless part of the stress tensor[29].

If one solves for the homogeneous deformation[30] of a rod of circular cross section, the only nonzero element of the stress tensor is $\sigma_{zz} = p$, where p is the pressure on either of the circular faces of the rod. One then finds that $\varepsilon_{xx} = \varepsilon_{yy} = \big(\frac{1}{9K} - \frac{1}{6\mu}\big)p$ and $\varepsilon_{zz} = \big(\frac{1}{9K} + \frac{1}{3\mu}\big)p$ are the only nonzero elements of the strain tensor. Thus,

$$Y \equiv \frac{\sigma_{zz}}{\varepsilon_{zz}} = \frac{9K\mu}{3K+\mu} \qquad , \qquad \beta \equiv -\frac{\varepsilon_{xx}}{\varepsilon_{zz}} = \frac{3K-2\mu}{2(3K+\mu)} \quad . \tag{6.78}$$

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[27] Integrate the differential torque $d\boldsymbol{N} = \boldsymbol{r}\times d\boldsymbol{F}$ over the entire body. Integrating by parts, one obtains a surface term and a volume term. The volume torque density is $-\epsilon_{ijk}\,\sigma_{jk}$, which must vanish, thereby entailing the symmetry $\sigma = \sigma^{\mathsf{T}}$.

[28] If you were wondering why we've suddenly switched to roman indices C_{ijkl} instead of Greek $C_{\alpha\beta\mu\nu}$, it is to obviate any confusion with the Lamé parameter μ.

[29] In d space dimensions, one has $K = \lambda + 2d^{-1}\mu$ and $\widetilde{m} = m - d^{-1}\mathsf{Tr}\,m$ is the traceless part of any matrix m.

[30] In a homogeneous deformation, the strain and stress tensors are constant throughout the body.

The quantity Y is called the *Young's modulus*, and must be positive. The quantity β is the *Poisson ratio* β and satisfies $\beta \in \big[-1, \frac{3}{2}\big]$. A material like tungsten carbide has a very large Young's modulus of $Y = 53.4 \times 10^{11}\,\text{dyn/cm}^2$ at STP, which means that you have to pull like hell in order to get it to stretch a little. Normally, when you stretch a material, it narrows in the transverse directions, which corresponds to a positive Poisson ratio. Materials for which $\beta < 0$ are called *auxetics*. When stretched, an auxetic becomes thicker in the directions perpendicular to the applied force. Examples include various porous foams and artificial macrostructures.

Elasticity and symmetry

Since

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij} \quad , \tag{6.79}$$

we may use the composite index notation in Tab. 6.15 to write the rank four tensor $C_{ijkl} \equiv C_{ab} = C_{ba}$ as a symmetric 6×6 matrix, with 21 independent elements before accounting for symmetry considerations. The linear stress-strain relation is then given by

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ 2\varepsilon_4 \\ 2\varepsilon_5 \\ 2\varepsilon_6 \end{pmatrix} \quad . \tag{6.80}$$

Since the elastic tensor is rank four, it is symmetric under inversion.

And now, let the symmetry commence!

- For triclinic crystals with point group C_1 or C_i, there are no symmetries to apply to C_{ab}, hence there are 21 independent elastic moduli. However, one can always rotate axes, and given the freedom to choose three Euler angles, this means we can always choose axes in such a way that three of the 21 moduli vanish, leaving 18. Again, this requires a nongeneric choice of axes.

- For monoclinic crystals, there is symmetry under $z \to -z$, and as in the example of the piezoelectric tensor $d_{\mu\nu\lambda}$, we have that C_{ijkl} vanishes if the index 3(z) appears an odd number of times, which means, in composite index notation,

  $$C_{14} = C_{15} = C_{24} = C_{25} = C_{34} = C_{35} = C_{46} = C_{56} = 0 \quad , \tag{6.81}$$

  leaving 13 independent elastic moduli for point groups C_2, C_s, and C_{2h}. The 6×6 matrix C_{ab} thus takes the form

  $$C^{\textsf{MONO}}_{ab} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{22} & C_{23} & 0 & 0 & C_{26} \\ C_{13} & C_{23} & C_{33} & 0 & 0 & C_{36} \\ 0 & 0 & 0 & C_{44} & C_{45} & 0 \\ 0 & 0 & 0 & C_{45} & C_{55} & 0 \\ C_{16} & C_{26} & C_{36} & 0 & 0 & C_{66} \end{pmatrix} \quad . \tag{6.82}$$

- For orthorhombic crystals, $x \to -x$ and $y \to -y$ are each symmetries. Adding $z \to -z$ in the case of D_{2h} doesn't buy us any new restrictions since C is symmetric under inversion. We then have $C_{ab} = 0$ whenever $a \in \{1,2,3\}$ and $b \in \{4,5,6\}$. The general form of C_{ab} is then

$$C^{\textsf{ORTHO}}_{ab} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \quad . \tag{6.83}$$

- For the tetragonal system, we can rotate (x, y, z) to $(-y, x, z)$. For the lower symmetry point groups among this system, namely C_4, S_4, and C_{4h}, the most general form is

$$C^{\textsf{TET}}_{ab}[C_4, S_4, C_{4h}] = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & -C_{16} & 0 & 0 & 0 & C_{66} \end{pmatrix} \quad , \tag{6.84}$$

  which has seven independent moduli. For the higher symmetry tetragonal point groups D_4, C_{4v}, D_{2d}, and D_{4h}, we have $C_{16} = 0$ because of the twofold axes which send (x, y, z) into $(x, -y, -z)$ and $(-x, y, -z)$, and there are only six independent moduli.

- For the trigonal point groups, our lives are again complicated by the C_3 rotations. One convenient way to deal with this is to define $\xi \equiv x + iy$ and $\bar{\xi} \equiv x - iy$, with

$$\begin{aligned} \varepsilon_{\xi\xi} &= \xi_i\, \xi_j\, \varepsilon_{ij} = \varepsilon_{xx} - \varepsilon_{yy} + 2i\, \varepsilon_{xy} \\ \varepsilon_{\xi\bar{\xi}} &= \xi_i\, \bar{\xi}_j\, \varepsilon_{ij} = \varepsilon_{xx} + \varepsilon_{xy} \\ \varepsilon_{z\xi} &= \xi_i\, \varepsilon_{zi} = \varepsilon_{zx} + i\, \varepsilon_{zy} \\ \varepsilon_{z\bar{\xi}} &= \bar{\xi}_i\, \varepsilon_{zi} = \varepsilon_{zx} - i\, \varepsilon_{zy} \quad , \end{aligned} \tag{6.85}$$

  where $\xi_i = \partial_i \xi$ where $x_1 = x$ and $x_2 = y$, and $\bar{\xi}_i = \partial_i \bar{\xi}$. A C_3 rotation then takes $\xi \to e^{2\pi i/3}\, \xi$ and $\bar{\xi} \to e^{-2\pi i/3}\, \bar{\xi}$. The only allowed elements of C_{ijkl} are

$$C_{zzzz} \quad , \quad C_{zz\xi\bar{\xi}} \quad , \quad C_{\xi\xi\bar{\xi}\bar{\xi}} \quad , \quad C_{\xi\bar{\xi}\xi\bar{\xi}} \quad , \quad C_{z\xi z\bar{\xi}} \quad , \quad C_{z\xi\xi\xi} \quad , \quad C_{z\bar{\xi}\bar{\xi}\bar{\xi}} \quad , \tag{6.86}$$

  and their corresponding elements obtained by permuting $C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}$. The first five of these are real, and the last two are complex conjugates: $C_{z\bar{\xi}\bar{\xi}\bar{\xi}} = C^*_{z\xi\xi\xi}$. So there are seven independent elastic moduli for the point groups C_3 and S_6. Note the general rule that we must have either no complex indices, one ξ and one $\bar{\xi}$ index, two each of ξ and $\bar{\xi}$, three ξ, or three $\bar{\xi}$. All other coefficients vanish by C_3 symmetry. We may now construct the elastic free energy density,

$$\begin{aligned} f = f_0 + \tfrac{1}{2} C_{zzzz}\, \varepsilon^2_{zz} + C_{\xi\xi\bar{\xi}\bar{\xi}}\, \varepsilon_{\xi\xi}\, \varepsilon_{\bar{\xi}\bar{\xi}} + 2\, C_{\xi\bar{\xi}\xi\bar{\xi}}\, \varepsilon^2_{\xi\bar{\xi}} + 2\, C_{zz\xi\bar{\xi}}\, \varepsilon_{zz}\, \varepsilon_{\xi\bar{\xi}} \\ + 4\, C_{z\xi z\bar{\xi}}\, \varepsilon_{z\xi}\, \varepsilon_{z\bar{\xi}} + 2\, C_{z\xi\xi\xi}\, \varepsilon_{z\xi}\, \varepsilon_{\xi\xi} + 2\, C_{z\bar{\xi}\bar{\xi}\bar{\xi}}\, \varepsilon_{z\bar{\xi}}\, \varepsilon_{\bar{\xi}\bar{\xi}} \quad . \end{aligned} \tag{6.87}$$

Note the coefficient of four in front of the $C_{z\xi z\bar{\xi}}$ term, which arises from summing over the eight equal contributions,

$$\tfrac{1}{2}\big(C_{z\xi z\bar{\xi}} + C_{z\xi\bar{\xi}z} + C_{\xi zz\bar{\xi}} + C_{\xi z\bar{\xi}z} + C_{z\bar{\xi}z\xi} + C_{z\bar{\xi}\xi z} + C_{\bar{\xi}zz\xi} + C_{\bar{\xi}z\xi z}\big)\, \varepsilon_{z\xi}\, \varepsilon_{z\bar{\xi}} = 4\, C_{z\xi z\bar{\xi}}\, \varepsilon_{z\xi}\, \varepsilon_{z\bar{\xi}} \quad . \tag{6.88}$$

From the free energy, one can identify the coefficients of $\varepsilon_a\, \varepsilon_b$, where a and b are composite indices, and thereby determine the general form for C_{ab}, which is

$$C^{\mathsf{TRIG}}_{ab}[C_3, S_6] = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & -C_{25} & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & C_{25} & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & C_{25} \\ -C_{25} & C_{25} & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & C_{25} & C_{14} & \frac{1}{2}(C_{11} - C_{12}) \end{pmatrix} \quad , \tag{6.89}$$

Adding in reflections or twofold axes, as we have in the higher symmetry groups in this system, *i.e.* D_3, C_{3v}, and D_{3d} allows for $\xi \leftrightarrow \bar{\xi}$, in which case $C_{z\xi\xi\xi} = C_{z\bar{\xi}\bar{\xi}\bar{\xi}}$, reducing the number of independent moduli to six, with $C_{25} = 0$.

There's another way to compute the number of independent moduli, using Eqn. 6.44. This applies to all cases, but it is particularly instructive to work it out for C_3 since the threefold rotations make its analysis more tedious than other cases where the symmetry operations merely permute the Cartesian indices. We start by decomposing the representation by which the symmetric rank two tensor ε_{ij} transforms into IRREPs of C_3. From Tab. 6.11, we have that $1 = A \oplus E \oplus E^*$, where 1 denotes the vector ($l = 1$) IRREP of $\mathsf{O}(3)$. Since the strain tensor ε is symmetric, we decompose $\varGamma_\varepsilon \equiv (1 \times 1)^{\mathsf{sym}}$ into C_3 IRREPs using $\chi^{\mathsf{sym}}(g) = \frac{1}{2}\big[\chi(g)\big]^2 + \frac{1}{2}\,\chi(g^2)$, according to which $\chi^{\varGamma_\varepsilon}(E) = 6$ and $\chi^{\varGamma_\varepsilon}(C_3) = \chi^{\varGamma_\varepsilon}(C_3^2) = 0$. Thus we have $\varGamma_\varepsilon = 2A \oplus 2E \oplus 2E^*$, whose total dimension is six, as is appropriate for a symmetric 3×3 matrix. We next must decompose $\varGamma_C \equiv (\varGamma_\varepsilon \times \varGamma_\varepsilon)^{\mathsf{sym}}$. into C_3 IRREPs. But this is a snap since we've computed the characters for $\varGamma_\varepsilon$[31]. Accordingly, we have $\chi^{\varGamma_C}(E) = \frac{1}{2}\big[\chi^{\varGamma_\varepsilon}(E)\big]^2 + \frac{1}{2}\chi^{\varGamma_\varepsilon}(E^2) = \frac{1}{2}\cdot 6^2 + \frac{1}{2}\cdot 6 = 21$ and $\chi^{\varGamma_C}(C_3) = \chi^{\varGamma_C}(C_3^2) = 0$. Therefore $\varGamma_C = 7A \oplus 7E \oplus 7E^*$ and we conclude from $n_A(\varGamma) = 7$ that there are seven independent elastic constants for C_3.

- For all seven hexagonal system point groups, we have $C_{z\xi\xi\xi} = C_{z\bar{\xi}\bar{\xi}\bar{\xi}} = 0$, because C_6 rotations take ξ to $\xi\, e^{i\pi/3}$, hence $C_{z\xi\xi\xi}$ to $-C_{z\xi\xi\xi}$. C_{3h} and D_{3h} don't contain this element, but do contain the mirror reflection $z \to -z$, hence in all cases the elastic tensor resembles that for the trigonal case, but with $C_{14} = C_{25} = 0$. Hence there are five independent moduli, with

$$C^{\mathsf{HEX}}_{ab} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) \end{pmatrix} \quad , \tag{6.90}$$

---

[31] We work directly with the reducible representation $\varGamma_\varepsilon$ and only decompose into C_3 IRREPs at the end of our calculation.

- For the cubic system (five point groups), the only independent elements are C_{xxxx}, C_{xxyy}, C_{xyxy}, and their symmetry-related counterparts such as C_{zzzz}, C_{yzyz}, *etc.* Thus,

$$C^{\mathsf{CUB}}_{ab} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \quad , \tag{6.91}$$

- For an isotropic material, $C_{11} = C_{22} + 2C_{44}$. The Lamé parameters are $\lambda = C_{12}$ and $\mu = C_{44}$.

6.3.7 Summary of tensor properties of the crystallographic point groups

At this point in the notes, we pause for a lengthy table, Tab. 6.16.

6.4 Vibrational and Electronic States of Molecules

6.4.1 Small oscillations of molecules

In §2.6 we considered the planar oscillations of a linear triatomic molecule of C_{3v} symmetry. We now consider the general case. First we consider the classical problem of N interacting point masses. Expanding the potential energy about equilibrium, the Hamiltonian is

$$H = \sum_{i,\alpha} \frac{(p_i^\alpha)^2}{2m_i} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \varPhi^{\alpha\beta}_{ij} \, u_i^\alpha \, u_j^\beta + \mathcal{O}(u^3) \quad , \tag{6.92}$$

where $\boldsymbol{u}_i$ is the vector displacement of ion i from its equilibrium position, $\boldsymbol{p}_i$ is its momentum, and m_i its mass. The indices α and β range over $\{1, \ldots, d\}$, where d is the dimension of space. The quantity $\varPhi^{\alpha\beta}_{ij}$ is known as the *dynamical matrix*, and it is defined to be

$$\varPhi^{\alpha\beta}_{ij} = \frac{\partial^2 V}{\partial u_i^\alpha \, \partial u_j^\beta}\bigg|_{\mathsf{EQ}} \quad , \tag{6.93}$$

where $V = V(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ is the potential, and $\boldsymbol{r}_j = \boldsymbol{r}_j^0 + \boldsymbol{u}_j$ with $\boldsymbol{r}_j^0$ the equilibrium position of the j^{th} ion. We now make a simple canonical transformation $p_i^\alpha = m_i^{1/2} \, \tilde{p}_i^\alpha$ and $u_i^\alpha = m_i^{-1/2} \tilde{u}_i^\alpha$ for all i and α. Clearly this preserves the Poisson bracket $\{u_i^\alpha \, , \, p_j^\beta\}_{\mathsf{PB}} = \delta_{ij} \, \delta^{\alpha\beta}$. The Hamiltonian is then

$$H = \sum_{i,\alpha} \frac{(\tilde{p}_i^\alpha)^2}{2} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \tilde{\varPhi}^{\alpha\beta}_{ij} \, \tilde{u}_i^\alpha \, \tilde{u}_j^\beta + \mathcal{O}(u^3) \quad , \tag{6.94}$$

	group symbol		tensor order			
crystal system	Schoenflies	HM	1^{st}	2^{nd}	3^{rd}	4^{th}
triclinic	C_1	1	3	6	18	21
	S_2	$\overline{1}$	0	6	0	21
monoclinic	C_2	2	1	4	8	13
	C_{1h}	m	2	4	10	13
	C_{2h}	$2/m$	0	4	0	13
orthorhombic	D_2	222	0	3	3	9
	C_{2v}	$mm2$	1	3	5	9
	D_{2h}	mmm	0	3	0	9
tetragonal	C_4	4	1	2	4	7
	S_4	$\overline{4}$	0	2	4	7
	C_{4h}	$4/m$	0	2	0	7
	D_4	422	0	2	1	6
	C_{4v}	$4mm$	1	2	3	6
	D_{2d}	$\overline{4}2m$	0	2	2	6
	D_{4h}	$4/mmm$	0	2	0	6
trigonal	C_3	3	1	2	6	7
	S_6	$\overline{3}$	0	2	0	7
	D_3	32	0	2	2	6
	C_{3v}	$3m$	1	2	4	6
	D_{3d}	$\overline{3}m$	0	2	0	6
hexagonal	C_6	6	1	2	4	5
	C_{3h}	$\overline{6}$	0	2	2	5
	C_{6h}	$6/m$	0	2	0	5
	D_6	622	0	2	1	5
	C_{6v}	$6mm$	1	2	3	5
	D_{3h}	$\overline{6}m2$	0	2	1	5
	D_{6h}	$6/mmm$	0	2	0	5
cubic	T	23	0	1	1	3
	T_h	$m\overline{3}$	0	1	0	3
	O	432	0	1	0	3
	T_d	$\overline{4}3m$	0	1	1	3
	O_h	$m\overline{3}m$	0	1	0	3
isotropic			0	1	0	2

Table 6.16: Tensor properties of the 32 crystallographic point groups.

where $\tilde{\varPhi}^{\alpha\beta}_{ij} = m_i^{-1/2} \varPhi^{\alpha\beta}_{ij} m_j^{-1/2}$ remains a real symmetric matrix in the composite indices $(i\alpha)$ and $(j\beta)$ and can therefore be diagonalized by an orthogonal transformation $S_{\sigma,i\alpha}$, where $\sigma \in \{1, \ldots, dN\}$ indexes the normal modes of the molecule. That means

$$\sum_{i,\alpha,j\beta} S_{\sigma,i\alpha}\, \tilde{\varPhi}^{\alpha\beta}_{ij}\, S^{\mathsf{T}}_{j\beta,\sigma'} = \omega^2_\sigma\, \delta_{\sigma\sigma'} \quad , \tag{6.95}$$

where ω_σ has the dimensions of T^{-2}, *i.e.* frequency squared[32]. If the equilibrium is a stable one, then $\omega^2_\sigma \geq 0$ for all σ. This orthogonal transformation induces a second canonical transformation, from $\{\tilde{u}_{i\alpha}, \tilde{p}_{i\alpha}\}$ to $\{\xi_\sigma, \pi_\sigma\}$, with

$$\xi_\sigma = S_{\sigma,i\alpha}\, \tilde{u}^\alpha_i \qquad , \qquad \pi_\sigma = \tilde{p}^\alpha_i\, S^{-1}_{i\alpha,\sigma} = S_{\sigma,i\alpha}\, \tilde{p}^\alpha_i \quad , \tag{6.96}$$

and the final form of the Hamiltonian is then

$$H = \sum_{\sigma=1}^{dN} \left(\tfrac{1}{2}\pi^2_\sigma + \tfrac{1}{2}\omega^2_\sigma\, \xi^2_\sigma \right) \quad . \tag{6.97}$$

Hamilton's equations of motion, which are of course preserved by the canonical transformations, are then $\dot{\xi}_\sigma = \partial H / \partial \pi_\sigma = \pi_\sigma$ and $\dot{\pi}_\sigma = -\partial H / \partial \xi_\sigma = -\omega^2_\sigma\, \xi_\sigma$, hence $\ddot{\xi}_\sigma = -\omega^2_\sigma\, \xi_\sigma$ and ω_σ is the oscillation frequency for the normal mode label σ.

6.4.2 Group theory and the dynamical matrix

To solve the general small oscillations problem, one must diagonalize the symmetric matrix $\tilde{\varPhi}^{\alpha\beta}_{ij}$, which is of rank dN. While today this is a simple computational task, even for large molecules, such crank-turning is oblivious to the consequences of point group symmetries that are relevant to many physically relevant cases. The resulting multiplet structure in the spectrum is inscrutable without group theory.

To determine the IRREPs of the molecular point group $\mathcal{P}$ under which energy multiplets transform, just follow these simple steps:

(i) First, identify the point group $\mathcal{P}$ which describes the full symmetry of the equilibrium configuration.

(ii) Second, construct for each element $g \in \mathcal{P}$ the *permutation matrix* $D^{\mathsf{per}}(g)$, defined to be

$$D^{\mathsf{per}}_{ij}(g) = \langle\, i \,|\, g \,|\, j \,\rangle = \begin{cases} 1 & \text{if } g \text{ takes ion } j \text{ to ion } i \\ 0 & \text{otherwise} \quad . \end{cases} \tag{6.98}$$

These matrices, which are all rank N, form a representation which we call $\varGamma^{\mathsf{per}}$.

(iii) Find the characters $\chi^{\mathsf{per}}(g)$. Note that

$$\chi^{\mathsf{per}}(g) = \text{number of ions remaining invariant under the operation } g \tag{6.99}$$

can be ascertained without computing all the matrix elements of $D^{\mathsf{per}}_{ij}(g)$.

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[32] The original $\varPhi^{\alpha\beta}_{ij}$ had dimensions of $EL^{-2} = MT^{-2}$, hence $\tilde{\varPhi}^{\alpha\beta}_{ij}$ has dimensions of T^{-2}.

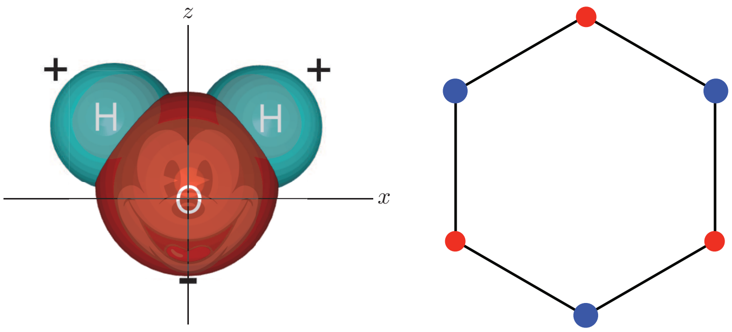

Figure 6.11: Left panel: the water molecule. Right panel: a molecule with C_{3v} symmetry. Rotations by an odd multiple of 60° are not a symmetry. Image credits: NCLab.com and ClipArtPanda.com.

(iv) For each $g \in \mathcal{P}$, construct the matrices $D^{\mathsf{vec}}(g) \in O(d)$, which is the $d \times d$ orthogonal matrix corresponding to the symmetry operation g.

(v) The symmetry operations operate on both the ion labels as well as their displacements from equilibrium. The corresponding representation of $\mathcal{P}$ is thus $\varPsi = \varGamma^{\mathsf{vec}} \times \varGamma^{\mathsf{per}}$. From this, we must subtract one copy of $\varGamma^{\mathsf{vec}}$ corresponding to translational zero modes, and one copy of $\varGamma^{\mathsf{rot}}$, corresponding to rotational zero modes. Note that $\varGamma^{\mathsf{rot}}$ is the 1^+ representation of $\mathsf{O}(3)$, whose matrices are given by $D^{\mathsf{rot}}(g) = \mathsf{det}\big[D^{\mathsf{vec}}(g)\big] \cdot D^{\mathsf{vec}}(g)$

(vi) To find the IRREPs for the $d(N-2)$ finite frequency vibrational modes, decompose $\varGamma^{\mathsf{per}}$, $\varGamma^{\mathsf{vec}}$, and $\varGamma^{\mathsf{rot}}$ into IRREPs of $\mathcal{P}$. The vibrational representations of the molecule are then given by

$$\varGamma^{\mathsf{vib}} = \overbrace{\varGamma^{\mathsf{vec}} \times \varGamma^{\mathsf{per}}}^{\varPsi} - \varGamma^{\mathsf{vec}} - \varGamma^{\mathsf{rot}} \quad . \tag{6.100}$$

(vii) Starting with an arbitrary (*e.g.* random) vector ψ, one can project onto the IRREPs $\varGamma$ contained in $\varGamma^{\mathsf{vib}}$ using the projectors

$$\varPi^{\varGamma} = \frac{d_{\varGamma}}{N_G} \sum_{g \in G} \chi^{\varGamma^*}(g)\, D^{\varPsi}(g) \qquad \text{or} \qquad \varPi^{\varGamma}_{\mu\nu} = \frac{d_{\varGamma}}{N_G} \sum_{g \in G} D^{\varGamma^*}_{\mu\nu}(g)\, D^{\varPsi}(g) \quad , \tag{6.101}$$

where $\varPi^{\varGamma}$ projects onto the IRREP $\varGamma$, and $\varPi^{\varGamma}_{\mu\nu}$ projects onto the μ^{th} row of $\varGamma$.

(viii) The projected vectors $\varPi^{\varGamma}\psi$ form a basis for all occurrences of the IRREP $\varGamma$ in the decomposition of the dN-dimensional representation $\varPsi$. One then must project out the zero modes in $\varGamma^{\mathsf{vec}}$ and $\varGamma^{\mathsf{rot}}$.

Water molecule

Let's test this scheme on the simple water molecule in Fig. 6.11. The group is C_{2v}, with elements E (identity), C_2 (rotation by π about z-axis), σ_v (reflection in x-z plane), and σ'_v (reflection in y-z plane):

$$C_2\,(x,y,z) = (-x,-y,z) \quad , \quad \sigma_v\,(x,y,z) = (x,-y,z) \quad , \quad \sigma'_v\,(x,y,z) = (-x,y,z) \quad . \tag{6.102}$$

Choosing the ion site labels O = 1, H = 2, and H′ = 3, the permutation matrices are

$$D^{\mathsf{per}}(E)=D^{\mathsf{per}}(\sigma_v)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\quad,\quad D^{\mathsf{per}}(C_2)=D^{\mathsf{per}}(\sigma_v')=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\quad,\tag{6.103}$$

which may readily be checked by inspection.

The matrices of $\varGamma^{\mathsf{vec}}$ are

$$\begin{gathered}D^{\mathsf{vec}}(E)=\begin{pmatrix}+1&0&0\\0&+1&0\\0&0&+1\end{pmatrix}\quad,\quad D^{\mathsf{vec}}(C_2)=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&+1\end{pmatrix}\\ D^{\mathsf{vec}}(\sigma_v)=\begin{pmatrix}+1&0&0\\0&-1&0\\0&0&+1\end{pmatrix}\quad,\quad D^{\mathsf{vec}}(\sigma_v')=\begin{pmatrix}-1&0&0\\0&+1&0\\0&0&+1\end{pmatrix}\quad.\end{gathered}\tag{6.104}$$

We may now compute the characters of the matrices $D^{\mathsf{per}}(g)$ and $D^{\mathsf{vec}}(g)$; they are reported in Tab. 6.17. Multiplying the characters to compute $\chi^{\varPsi}(g)=\chi^{\varGamma^{\mathsf{vec}}}(g)\,\chi^{\varGamma^{\mathsf{per}}}(g)$, and decomposing into IRREPs of C_{2v}, we find

$$\varPsi=\varGamma^{\mathsf{vec}}\times\varGamma^{\mathsf{per}}=3A_1\oplus A_2\oplus 3B_1\oplus 2B_2\quad.\tag{6.105}$$

From these IRREPs we must exclude

$$\begin{aligned}\varGamma^{\mathsf{vec}}&=A_1\oplus B_1\oplus B_2\\ \varGamma^{\mathsf{rot}}&=A_2\oplus B_1\oplus B_2\quad,\end{aligned}\tag{6.106}$$

resulting in

$$\varGamma^{\mathsf{vib}}=2A_1\oplus B_1\quad.\tag{6.107}$$

C_{2v}	E	C_2	σ_v	σ_v'	basis
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y
$\varGamma^{\mathsf{vec}}$	3	-1	1	1	$A_1\oplus B_1\oplus B_2$
$\varGamma^{\mathsf{rot}}$	3	-1	-1	-1	$A_2\oplus B_1\oplus B_2$
$\varGamma^{\mathsf{per}}$	3	1	3	1	$2A_1\oplus B_1$
$\varGamma^{\mathsf{vec}}\times\varGamma^{\mathsf{per}}$	9	-1	3	1	$3A_1\oplus A_2\oplus 3B_1\oplus 2B_2$

$\varGamma\times\varGamma'$	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

Table 6.17: Character and representation product tables for C_{2v}.

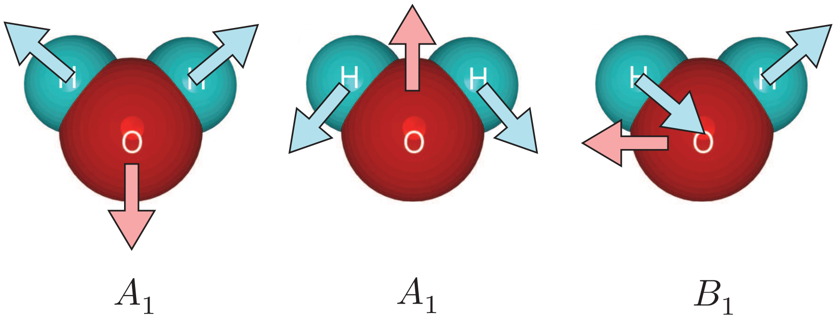

Figure 6.12: Normal modes of the H_2O molecule and their C_{2v} IRREP labels. Image credit: NCLab.com.

Recall we started with nine degrees of freedom for the water molecule, corresponding to three translations for each of its constituent atoms. Subtracting three translational and three rotational zero modes, we are left with three finite frequency vibrational modes, two of which transform according to A_1 and one according to B_1. These vibrations are depicted in Fig. 6.12.

Buckyball

Flush with success after identifying the IRREPs or the vibrational spectrum of H_2O, let's try something with a bigger symmetry group – the buckyball C_{60}. The buckyball is depicted in Fig. 6.13. Its symmetry group is the icosahedral group with inversion, $I_h = I \times C_i$, which has 120 elements. A character tableis provided in Tab. 6.18. It should come as no surprise that $\Gamma^{\mathsf{vec}} = T_{1u}$ and $\Gamma^{\mathsf{rot}} = T_{1g}$.

When it comes to constructing Γ^{per}, we are in luck. Eight of the ten classes of symmetry operations leave no sites fixed, hence for these classes we have $\chi^{\mathsf{per}}(\mathcal{C}) = 0$. The only operations which leave fixed points are the identity, which leaves every site invariant, hence $\chi^{\mathsf{per}}(E) = 60$, and the reflections 15σ, each of which leaves four sites invariant, hence $\chi^{\mathsf{per}}(15\sigma) = 4$[33]. Taking the product with Γ^{vec} to form $\Psi = \Gamma^{\mathsf{vec}} \times \Gamma^{\mathsf{per}}$, we have $\chi^{\Psi}(E) = 180$ and $\chi^{\Psi}(15\sigma) = 4$, hence thus, the number of times each IRREP Γ appears in the product representation Ψ is

$$\begin{aligned} n_\Gamma(\Psi) &= \frac{1}{120}\Big(180 \cdot \chi^\Gamma(E) + 4 \cdot 15 \cdot \chi^\Gamma(15\sigma)\Big) \\ &= \tfrac{3}{2}\,\chi^\Gamma(E) + \tfrac{1}{2}\,\chi^\Gamma(15\sigma) \quad . \end{aligned} \tag{6.108}$$

The resulting $n_\Gamma(\Psi)$ values are given in the table within Fig. 6.13. Summing the dimensions of the IRREPs times their multiplicities, one finds

$$\sum_\Gamma n_\Gamma(\Psi)\, d_\Gamma = 180 \quad , \tag{6.109}$$

which is the total number of vibrational degrees of freedom of the buckyball (including zero modes). From the decomposition of Ψ into I_h IRREPs, one must subtract the translational and rotational zero

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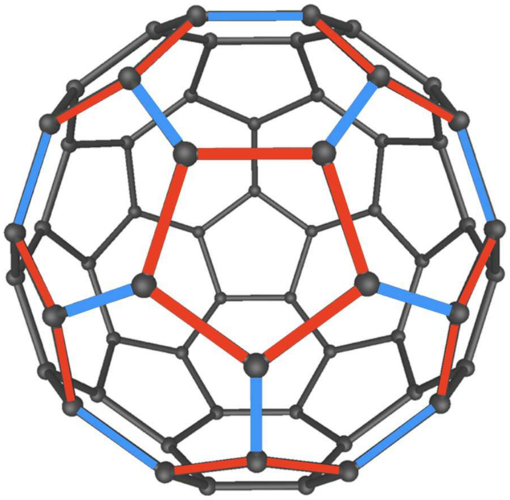
[33] See how a reflection plane bisecting the buckyball of Fig. 6.13 contains two links, *i.e.* four sites.



Γ	d_Γ	n_Γ	$n_\Gamma d_\Gamma$
A_g	1	2	2
T_{1g}	3	4	12
T_{2g}	3	4	12
G_g	4	6	24
H_g	5	8	40
A_u	1	1	1
T_{1u}	3	5	15
T_{2u}	3	5	15
G_u	4	6	24
H_u	5	7	35

Figure 6.13: The buckyball C_{60}, its IRREPs, and the decomposition of $\Psi = \Gamma^{\text{vec}} \times \Gamma^{\text{per}}$.

modes, which is to say one copy each of T_{1u} and T_{1g} , respectively. This leaves

$$\Gamma^{\text{vib}} = 2A_g \oplus 3T_{1g} \oplus 4T_{2g} \oplus 6G_g \oplus 8H_g \oplus A_u \oplus 4T_{1u} \oplus 5T_{2u} \oplus 6G_u \oplus 7H_u \quad . \tag{6.110}$$

Animations of each of these normal modes may be viewed at

http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm

6.4.3 Selection rules for infrared and Raman spectroscopy

Recall that electromagnetic radiation can excite modes via dipole transitions, and that a general matrix element of the form $\langle\, \Gamma_{\rm f}\, \beta \,|\, \hat{Q}^{\Gamma}_{\mu} \,|\, \Gamma_{\rm i}\, \alpha \,\rangle$ can be nonzero only if $\Gamma_{\rm f} \in \Gamma_{\rm i} \times \Gamma$. Usually the initial state is the ground state, in which case $\Gamma_{\rm i}$ is the trivial representation, and in our case $\Gamma = \Gamma^{\text{vec}}$, corresponding to an electric dipole transition. Then our condition for the possibility of a nonzero matrix element becomes simply $\Gamma_{\rm f} \in \Gamma^{\text{vec}}$. Such modes are said to be *IR-active*. For example, for H_2O, all three vibrational modes are IR-active, because $\Gamma^{\text{vib}} = 2A_1 \oplus B_1$ and $\Gamma^{\text{vec}} = A_1 \oplus B_1 \oplus B_2$. For C_{60}, only the five T_{1u} multiplets are IR-active.

Raman spectroscopy involves the detection of inelastically scattered light. Thus, there is an incoming electromagnetic wave $\boldsymbol{\mathcal{E}}_{\rm i}$ and an outgoing wave $\boldsymbol{\mathcal{E}}_{\rm f}$. These are coupled through a 3×3 symmetric polarization tensor, $\alpha_{\mu\nu}$. We shall therefore be interested in symmetric, rank-two tensor representations of the molecular point group $\mathcal{P}$.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	I	$12S_{10}^3$	$12S_{10}$	$20S_6$	15σ
A_g	1	1	1	1	1	1	1	1	1	1
T_{1g}	3	τ	$1-\tau$	0	-1	3	τ	$1-\tau$	0	-1
T_{2g}	3	$1-\tau$	τ	0	-1	3	$1-\tau$	τ	0	-1
G_g	4	-1	-1	1	0	4	-1	-1	1	0
H_g	5	0	0	-1	1	5	0	0	-1	1
A_u	1	1	1	1	1	-1	-1	-1	-1	-1
T_{1u}	3	τ	$1-\tau$	0	-1	-3	$-\tau$	$-1+\tau$	0	1
T_{2u}	3	$1-\tau$	τ	0	-1	-3	$-1+\tau$	$-\tau$	0	1
G_u	4	-1	-1	1	0	-4	1	1	-1	0
H_u	5	0	0	-1	1	-5	0	0	1	-1
Γ^{vec}	3	τ	$1-\tau$	0	-1	-3	$-\tau$	$-1+\tau$	0	1
Γ^{rot}	3	τ	$1-\tau$	0	-1	3	τ	$1-\tau$	0	-1
Γ^{per}	60	0	0	0	0	0	0	0	0	4
Ψ	180	0	0	0	0	0	0	0	0	4

Table 6.18: Character table for the icosahedral group $I_{\rm h}$. Note $\tau = 2\cos\frac{\pi}{5} = \frac{1}{2}\big(1+\sqrt{5}\,\big)$ satisfies $\tau^2 = 1+\tau$. Γ^{per} is the permutation representation for the buckyball C_{60}.

The derivation of the effective Raman Hamiltonian is somewhat involved, and we include here a brief discussion for the sake of completeness. The goal is to compute the effective molecular Hamiltonian up to second order in the external *time-dependent* electric field $\boldsymbol{\mathcal{E}}(t)$, within a restricted manifold of molecular states consisting of the ground state $|\,{\rm g}\,\rangle$, assumed to transform trivially under point group operations, and an excited state multiplet $|\,\Gamma\,\gamma\,\rangle$, where γ is the partner label, transforming as the IRREP Γ. The effective Hamiltonian is found to be[34]

$$\hat{H}_{\rm eff}(t) = \hat{H}_0 - \hat{\boldsymbol{\mu}}\cdot\boldsymbol{\mathcal{E}}(t) + \tfrac{1}{2}\,\mathcal{E}_\rho(t)\int\limits_{-\infty}^{t}\!dt'\;\hat{\alpha}_{\rho\lambda}(t-t')\,\mathcal{E}_\lambda(t') + \mathcal{O}(\mathcal{E}^3) \quad , \tag{6.111}$$

where

$$\hat{H}_0 = E_{\rm g}\,|\,{\rm g}\,\rangle\langle\,{\rm g}\,| + {\sum_\Gamma}' E_\Gamma \sum_{\gamma=1}^{d_\Gamma} |\,\Gamma\,\gamma\,\rangle\langle\,\Gamma\,\gamma\,| \tag{6.112}$$

includes the molecular ground state and all vibrational excitation multiplets, and

$$\hat{\boldsymbol{\mu}} = -e\sum_{a,b} |\,b\,\rangle\,\langle\,b\,|\,\hat{\boldsymbol{d}}\,|\,a\,\rangle\,\langle\,a\,| \quad , \tag{6.113}$$

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[34] See, *e.g.*, chapter 4 of R. Long, *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules* (Wiley, 2002).

where $|\,a\,\rangle$ and $|\,b\,\rangle$ are taken from the low-lying states $|\,\mathrm{g}\,\rangle$ and $|\,\Gamma\,\gamma\,\rangle$, and $\hat{\boldsymbol{d}}$ is the dipole moment operator of the molecule. If the molecular point group $\mathcal{P}$ contains the inversion element I, then $\hat{\boldsymbol{d}}$ can only have matrix elements between representations of different parity. The second order term involves the polarization tensor, which is obtained from time-dependent perturbation theory, *viz.*

$$\hat{\alpha}_{\rho\lambda}(s) = \frac{i}{\hbar}\Big[\hat{P}\,e^{i\hat{H}_0 s/\hbar}\,\hat{d}_\rho\,e^{-i\hat{H}_0 s/\hbar}\,\hat{Q}\,\hat{d}_\lambda\,\hat{P} - \hat{P}\,\hat{d}_\lambda\,\hat{Q}\;e^{i\hat{H}_0 s/\hbar}\,\hat{d}_\rho\,e^{-i\hat{H}_0 s/\hbar}\,\hat{P}\Big]\,\Theta(s) \quad , \tag{6.114}$$

where $\hat{P} = \sum_a |\,a\,\rangle\langle\,a\,|$ is the projector onto the ground state and low-lying vibrational multiplets, and $\hat{Q} \equiv \hat{\mathbb{1}} - \hat{P} = \sum'_m |\,m\,\rangle\langle\,m\,|$ is the orthogonal projector onto all other eigenstates (hence the prime on the sum) of the $\boldsymbol{\mathcal{E}} = 0$ molecular Hamiltonian. $\Theta(s)$ is the step function. The Fourier transform of $\hat{H}_{\text{eff}}(t)$ is

$$\hat{H}_{\text{eff}}(\omega) = \hat{H}_0\,\delta(\omega) - \boldsymbol{\mathcal{E}}(\omega)\cdot\hat{\boldsymbol{\mu}} + \tfrac{1}{2}\int\limits_{-\infty}^{\infty}\!\frac{d\omega'}{2\pi}\,\mathcal{E}_\rho(\omega-\omega')\,\mathcal{E}_\lambda(\omega')\,\hat{\alpha}_{\rho\lambda}(\omega') \quad , \tag{6.115}$$

where

$$\hat{\alpha}_{\rho\lambda}(\omega) = \sum_{a,b}\sum_n{}'\,|\,b\,\rangle\left\{\frac{\langle\,b\,|\,\hat{d}_\rho\,|\,n\,\rangle\langle\,n\,|\,\hat{d}_\lambda\,|\,a\,\rangle}{E_n - E_b - \hbar\omega - i0^+} + \frac{\langle\,b\,|\,\hat{d}_\lambda\,|\,n\,\rangle\langle\,n\,|\,\hat{d}_\rho\,|\,a\,\rangle}{E_n - E_a + \hbar\omega + i0^+}\right\}\langle\,a\,| \quad . \tag{6.116}$$

To be clear about what it is we are doing here, we are endeavoring to derive a low-energy effective Hamiltonian for the vibrational states of a molecule. In general a given molecular state has electronic, vibrational, and rotational quantum numbers. In many relevant cases, there is a hierarchy of energy scales, with $\Delta E_{\text{rot}} \ll \Delta E_{\text{vib}} \ll \hbar\omega \ll \Delta E_{\text{el}}$, which we shall assume. We'll ignore here the rotational modes, *i.e.* we'll treat them as zero modes of the vibrational spectrum. All states may be decomposed as

$$|\,n\,\rangle = |\,\mathrm{v}_n\,\rangle \otimes |\,\mathrm{e}_n\,\rangle \quad , \tag{6.117}$$

i.e. into a direct product of nuclear coordinate (vibrational) and electronic wavefunctions, where the electronic wavefunctions are eigenfunctions of the Born-Oppenheimer Hamiltonian in which the nuclear coordinates are frozen. Thus $|\,\mathrm{e}_n\,\rangle = |\,\mathrm{e}_n(Q)\,\rangle$ depends explicitly on the nuclear coordinates. Although the Born-Oppenheimer energies $E^{\mathsf{BO}}_n(Q)$ will then depend on Q, the electronic energies dominate and we may take $E^{\mathsf{BO}}_n(Q) \approx E^{\mathsf{BO}}_n(Q^0)$ at the equilibrium nuclear coordinates. The dipole moment operator $\hat{\boldsymbol{d}} = -e\sum_{i,l}\boldsymbol{r}_{i,l}$ is a sum over electron displacements with respect to the fixed origin of the point group,where $\boldsymbol{r}_{i,l}$ for a given electron is a sum of terms including the equilibrium position $\boldsymbol{Q}^0_i$ of the i^{th} ion, its displacement $\boldsymbol{u}_i = \boldsymbol{Q}_i - \boldsymbol{Q}^0_i$ from equilibrium, and the electronic position $\boldsymbol{\xi}_{i,l}$ of the l^{th} electron on that ion with respect to its nucleus. We may now write[35]

$$\begin{aligned}\hat{\alpha}_{\rho\lambda}(Q,\omega) = \frac{1}{\hbar}\sum_n{}'\Bigg\{&\frac{\langle\,\mathrm{e_g}(Q)\,|\,\hat{d}_\rho\,|\,\mathrm{e}_n(Q)\,\rangle\langle\,\mathrm{e}_n(Q)\,|\,\hat{d}_\lambda\,|\,\mathrm{e_g}(Q)\,\rangle}{\omega_{n\mathrm{g}} - \omega - i0^+}\\ &+\frac{\langle\,\mathrm{e_g}(Q)\,|\,\hat{d}_\lambda\,|\,\mathrm{e}_n(Q)\,\rangle\langle\,\mathrm{e}_n(Q)\,|\,\hat{d}_\rho\,|\,\mathrm{e_g}(Q)\,\rangle}{\omega_{n\mathrm{g}} + \omega + i0^+}\Bigg\} \quad ,\end{aligned} \tag{6.118}$$

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[35] In deriving Eqn. 6.118, we use the fact that the Q-dependent part of the energy $E_n(Q)$ may be dropped in the denominator because of the aforementioned energy scale hierarchy. We may then collapse the sum on the vibrational component of the high energy excited states using completeness.

which acts as an operator on the vibrational wavefunctions $|\, v_a \,\rangle$. The matrix elements $\langle\, \mathrm{e_g}(Q) \,|\, \hat{d}_\rho \,|\, \mathrm{e}_n(Q) \,\rangle$ *etc.* involve integration over the electronic coordinates alone, and therefore are functions of the ionic coordinates Q. Similarly, we define

$$\hat{\mu}_\rho(Q) = -e \,\big\langle\, \mathrm{e_g}(Q) \,\big|\, \hat{d}_\rho \,\big|\, \mathrm{e_g}(Q) \,\big\rangle \quad . \tag{6.119}$$

We arrive at an effective time-dependent Hamiltonian for the low-lying vibrational levels, which when expressed in the frequency domain is[36]

$$\begin{aligned}\big\langle\, \mathrm{v}_b \,\big|\, \hat{H}_{\rm eff}(\omega) \,\big|\, \mathrm{v}_a \,\big\rangle &= E_a \,\delta_{ab}\, \delta(\omega) - \mathcal{E}_\rho(\omega) \,\big\langle\, \mathrm{v}_b \,\big|\, \hat{\mu}_\rho(Q) \,\big|\, \mathrm{v}_a \,\big\rangle \\ &\qquad + \tfrac{1}{2}\int\limits_{-\infty}^{\infty} \frac{d\omega'}{2\pi}\, \mathcal{E}^*_\rho(\omega'-\omega)\, \mathcal{E}_\lambda(\omega') \,\big\langle\, \mathrm{v}_b \,\big|\, \hat{\alpha}_{\rho\lambda}(Q,\omega') \,\big|\, \mathrm{v}_a \,\big\rangle \quad .\end{aligned} \tag{6.120}$$

Finally, if the wavefunctions can be taken to be real, we see from Eqn. 6.118 that the polarizability matrix is symmetric, *i.e.* $\alpha_{\rho\lambda}(Q,\omega) = \alpha_{\lambda\rho}(Q,\omega)$. Note that the nuclear part $|\, \mathrm{e_g}(Q) \,\rangle\langle\, \mathrm{e_g}(Q) \,|$ is a one-dimensional projector common to all terms in the effective vibrational Hamiltonian, and can hence be set to unity.

At this point the electric field $\mathcal{E}_\rho(\omega)$ may be quantized and written in terms of photon creation and annihilation operators. The second term corresponds to *Rayleigh scattering* in which a photon of frequency $\omega = (E_b - E_a)/\hbar$ is absorbed. We assume here that a is the ground state. If a represents an occupied excited state, as may be the case at finite temperature, a photon can be emitted. Regarding the third term in $\hat{H}_{\rm eff}$, which corresponds to Raman scattering, we can read off from the form of the Hamiltonian that if $\mathcal{E}_\lambda(\omega')$ destroys an incoming photon of frequency ω', then $\mathcal{E}^*_\rho(\omega'-\omega)$ creates an outgoing photon of frequency $\omega'-\omega$, where $\hbar\omega = E_b - E_a$. When $E_b > E_a$ this is called *Stokes scattering*. In Stokes scattering, the frequency of the emitted radiation is less than that of the incident radiation. When $E_b < E_a$, the emitted radiation is at a higher frequency, and the process is called *anti-Stokes* scattering[37].

For Rayleigh scattering, the selection rules are as we discussed above. The operator $\hat{\boldsymbol{\mu}}$ transforms as a vector, hence $\langle\, b \,|\, \hat{\boldsymbol{\mu}} \,|\, a \,\rangle$ can be nonzero only if $\varGamma_b \in \varGamma^{\sf vec} \times \varGamma_a$. For Raman scattering, $\hat{\alpha}_{\rho\lambda}$ transforms as the symmetric product of two vectors, *i.e.* as $\varPsi = (\varGamma^{\sf vec} \times \varGamma^{\sf vec})^{\sf sym}$. This representation is symmetric under inversion, hence Raman scattering does not result in a change of parity. Therefore, in molecules with inversion symmetry, IR (Rayleigh) and Raman scattering are complementary tools, since a mode can either be IR or Raman active, but not both. If there is no inversion symmetry, a mode can be both IR *and* Raman active. Of course, a mode can be inactive for both IR and Raman. Modes which are inactive for reasons other than parity are called *silent*.

As an example, consider our old friend C_{3v}, for which $\varGamma^{\sf vec} = A_1 \oplus E$, with $\chi^{\sf vec}(E) = 3$, $\chi^{\sf vec}(2C_3) = 0$, and $\chi^{\sf vec}(3\sigma_v) = 1$. From

$$\chi^{\sf sym}(g) = \tfrac{1}{2}\big[\chi^{\sf vec}(g)\big]^2 + \tfrac{1}{2}\chi^{\sf vec}(g^2) \quad , \tag{6.121}$$

we have $\chi^{\sf sym}(E) = 6$, $\chi^{\sf sym}(2C_3) = 0$, and $\chi^{\sf sym}(3\sigma_v) = 2$, whence the decomposition formula yields $\varGamma^{\sf sym} = 2A_1 \oplus 2E$. Thus, if the initial vibrational state is the ground state, the final state is Raman active if $\varGamma_{\rm f}$ is either A_1 or E but not A_2.

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[36] See also the discussion in the appendix, §6.8.

[37] Stokes' law says that the frequency of fluorescent light is always less than or equal to that of the incident light. Hence Stokes lines are those which correspond to Stokes' law, and anti-Stokes lines are those which violate it.

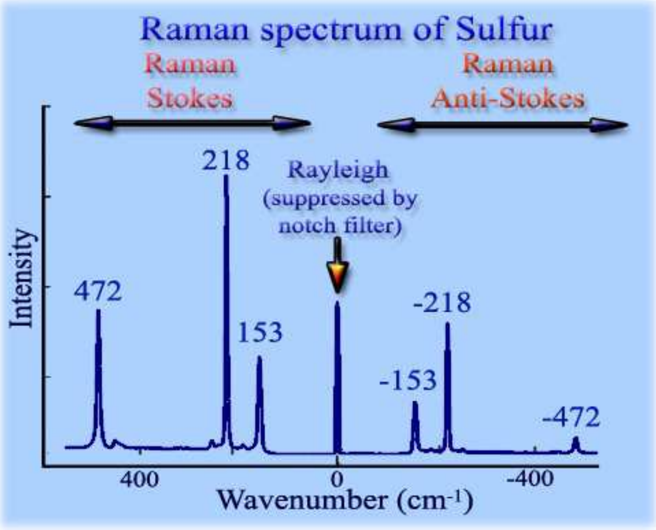

Figure 6.14: Rayleigh and Raman spectral lines in crystalline sulfur. Image credit: spectrometry316.blogspot.com.

For H_2O, with point group C_{2v}, we found $\mathit{\Gamma}^{\mathsf{vib}} = 2A_1 \oplus B_1$. We next need $\mathit{\Gamma}^{\mathsf{sym}}$, which we obtain by computing the characters $\chi^{\mathsf{sym}}(g)$ using Eqn. 6.121. Note that C_2, σ_v, and σ_v' are all of order two, and we obtain

$$\chi^{\mathsf{sym}}(E) = 6 \quad , \quad \chi^{\mathsf{sym}}(C_2) = \chi^{\mathsf{sym}}(\sigma_v) = \chi^{\mathsf{sym}}(\sigma_v') = 2 \quad . \tag{6.122}$$

Decomposing into C_{2v} IRREPs, we find

$$\mathit{\Gamma}^{\mathsf{sym}} = 3A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad , \tag{6.123}$$

the total dimension of which is six, corresponding to the degrees of freedom in a real 3×3 symmetric matrix. Thus, all IRREPs are present in $\mathit{\Gamma}^{\mathsf{sym}}$ and all modes are Raman active.

For the buckyball, $\mathit{\Gamma}^{\mathsf{vec}} = T_{1u}$, and one finds

$$I_h \,:\, \mathit{\Gamma}^{\mathsf{vec}} \times \mathit{\Gamma}^{\mathsf{vec}} = A_g \oplus T_{1g} \oplus H_g \quad . \tag{6.124}$$

The sum of the dimensions is nine, corresponding to a 3×3 real matrix. To obtain $\mathit{\Gamma}^{\mathsf{sym}}$, we must subtract out the antisymmetric tensor representation $\mathit{\Gamma}^{\mathrm{ASY}}$. Since this is of dimension three, we immediately know it must be T_{1g} and that $\mathit{\Gamma}^{\mathsf{sym}} = A_g \oplus H_g$, which is properly of total dimension six. Comparing with Fig. 6.13, we see that in addition to the Raman inactive parity-odd multiplets, all parity even multiplets other than A_g and H_g are Raman silent. A quick check of the character tables shows that the representation functions for T_{1g} are the angular momentum operators, which indeed correspond to an antisymmetric rank three tensor. But if this casual elimination of T_{1g} strikes one as too glib – even though it is obviously correct! – we can grind through a direct calculation using Eqn. 6.121 and Tab. 6.18. All we need to keep in mind is that $(C_5)^2 = C_5^2$, $(C_5^2)^2 = C_5^{-1}$ (class C_5), $(C_3)^2 = C_3^{-1}$ (class C_3), $I^2 = E$, $(S_{10}^3)^2 = C_5^3$ (class C_5^2), $(S_{10})^2 = C_5$, $(S_6)^2 = C_3$, and $\sigma^2 = 1$. It is then straightforward to derive

$$\chi^{\mathsf{sym}}(E) = \chi^{\mathsf{sym}}(I) = 6 \quad , \quad \chi^{\mathsf{sym}}(C_5) = \chi^{\mathsf{sym}}(S_{10}) = 1 \quad , \quad \chi^{\mathsf{sym}}(C_5^2) = \chi^{\mathsf{sym}}(S_{10}^3) = 1 \tag{6.125}$$

and

$$\chi^{\mathsf{sym}}(C_3) = \chi^{\mathsf{sym}}(S_6^3) = 0 \quad , \quad \chi^{\mathsf{sym}}(C_2) = \chi^{\mathsf{sym}}(\sigma) = 2 \quad . \tag{6.126}$$

One then derives the decomposition

$$n_\Gamma(\Gamma^{\mathsf{sym}}) = \frac{1}{10}\Big(\chi^\Gamma(E) + 2\,\chi^\Gamma(C_5) + 2\,\chi^\Gamma(C_5^2) + 5\,\chi^\Gamma(C_2)\Big) \quad , \tag{6.127}$$

from which one readily recovers $\Gamma^{\mathsf{sym}} = A_g \oplus H_g$.

6.4.4 Electronic spectra of molecules

The decomposition of electronic eigenstates follows the same general rubric as in §6.4.2, except rather than decomposing $\Gamma^{\mathsf{vec}} \times \Gamma^{\mathsf{per}}$, we must decompose $\Gamma^{\mathsf{orb}} \times \Gamma^{\mathsf{per}}$, where Γ^{orb} is the representation for the atomic orbitals. There are no translational or rotational zero modes to subtract.

Consider, for example, a benzene molecule, C_6H_6. The symmetry group is C_{6v}. Each carbon atom has a $1s^2\,2s^2$ core plus two electrons in the 2p orbital, one of which forms a bond with its neighboring hydrogen atom. The remaining six electrons are associated with the carbon p_z (π) orbitals. A p_z orbital is invariant under all C_{6v} operations, since it is oriented perpendicular to the symmetry plane. Thus, $\Gamma^{\mathsf{orb}} = A_1$ for benzene, and we are left with the task of decomposing Γ^{per}. The only symmetry operations which leave sites invariant are the identity, for which $\chi^{\mathsf{per}}(E) = 6$, and the diagonal mirrors, for which $\chi^{\mathsf{per}}(\sigma_d) = 2$. Consulting the character table for C_{6v}, one readily finds

$$\Gamma^{\mathsf{per}} = A_1 \oplus B_2 \oplus E_1 \oplus E_2 \quad . \tag{6.128}$$

A simple tight-binding model for the π orbitals is given by

$$\hat{H} = -t\sum_{n=1}^{6}\sum_{\sigma}\Big(\,|\, n,\sigma \,\rangle\langle\, n{+}1,\sigma \,| + |\, n{+}1,\sigma \,\rangle\langle\, n,\sigma \,|\,\Big) \quad , \tag{6.129}$$

which is instantly diagonalized in the crystal momentum basis as

$$\hat{H} = -2t\sum_{k,\sigma}\cos(nk)\,|\, k,\sigma \,\rangle\langle\, k,\sigma \,| \quad , \tag{6.130}$$

where $k = 0, \pm\frac{1}{3}\,\pi, \pm\frac{2}{3}\,\pi$, and π. Note that without spin-orbit coupling, the spin just comes along for the ride, and we needn't bother with the trouble of the double group. The eigenfunctions are

$$|\, k,\sigma \,\rangle = \frac{1}{\sqrt{6}}\sum_{n=1}^{6} e^{ikn}\,|\, n,\sigma \,\rangle \quad . \tag{6.131}$$

We see that the $k = 0$ and $k = \pi$ states are singly degenerate, hence one must transform as A_1 and one as B_2. Obviously $k = 0$ transforms as A_1, so $k = \pi$ must transform as B_2. Just to check, note that the mirrors σ_v which run perpendicular to the hexagonal faces, exchange odd and even numbered sites, while the diagonal mirrors preserve the oddness or evenness of the site index n. Since $\chi^{B_2}(\sigma_v) = -1$ and $\chi^{B_2}(\sigma_d) = +1$, we can be sure there was no mistake, and the $k = \pi$ state indeed transforms as

B_2. The remaining eigenstates are organized into two doublets: $k = \pm\frac{1}{3}\pi$ and $k = \pm\frac{2}{3}\pi$. A check of the C_{3v} character table tells us that $\chi^{E_{1,2}}(C_2) = \pm 2$, so we can use this as a test. Under C_2, we have $n \to n + 3$. Since $\exp(3ik) = -1$ for $k = \pm\frac{1}{3}\pi$, we conclude that this doublet transforms as E_1 and $k = \pm\frac{2}{3}\pi$ transforms as E_2.

Next, consider a cubic molecule. If we construct a tight-binding model consisting of s-orbitals on each site, there will be a total of eight orbitals for each spin polarization. How are they arranged in IRREPs of O_h? Simple. We first note that the only operations $g \in O_h$ which leave sites are invariant are the identity, which preserves all eight sites, the threefold rotations $8C_3$ about the four axes running diagonally through the cube, which preserve the two sites along each axis, and the diagonal mirrors $6IC_2'$, which preserve the four sites lying in each mirror plane. For every other class, $\chi^{\mathsf{per}}(\mathcal{C}) = 0$. Since the orbitals are all s-states, we have $\Gamma^{\mathsf{orb}} = A_{1g}$, the trivial representation. After consulting the character table for O_h, we find

$$\Gamma^{\mathsf{orb}} \times \Gamma^{\mathsf{per}} = A_{1g} \oplus T_{1g} \oplus A_{2u} \oplus T_{2u} \quad . \tag{6.132}$$

Suppose instead each site contained p-orbitals rather than an s-orbital. In this case, $\Gamma^{\mathsf{orb}} = \Gamma^{\mathsf{vec}}$, and the decomposition formula yields

$$\Gamma^{\mathsf{orb}} \times \Gamma^{\mathsf{per}} = A_{1g} \oplus E_g \oplus T_{1g} \oplus 2T_{2g} \oplus A_{2u} \oplus E_u \oplus 2T_{1u} \oplus T_{2u} \quad . \tag{6.133}$$

Adding up all the dimensions yields 24, which corresponds to the total number of orbitals, as required.

O_h	E	$8C_3$	$6IC_2'$	decomposition
Γ^{vec}	3	0	1	T_{1u}
Γ^{per}	8	2	4	$A_{1g} \oplus T_{1g} \oplus A_{2u} \oplus T_{2u}$
$\Gamma^{\mathsf{vec}} \times \Gamma^{\mathsf{per}}$	24	0	4	see text

Table 6.19: Partial character table for O_h. Classes shown are those for which $\chi^{\mathsf{per}}(\mathcal{C}) \neq 0$ for the cube.

6.5 Phonons in Crystals

Consider next the vibrations of a crystalline solid, which are called *phonons*. We define $\boldsymbol{R}$ to be a Bravais lattice vector, *i.e.* a label for a unit cell, and $\boldsymbol{u}_i(\boldsymbol{R})$ to be the displacement of the i^{th} basis ion in the $\boldsymbol{R}$ unit cell. The Hamiltonian is

$$H = \sum_{\boldsymbol{R},i} \frac{\boldsymbol{p}_i^2(\boldsymbol{R})}{2m_i} + \frac{1}{2} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{i,j} \sum_{\alpha,\beta} u_i^\alpha(\boldsymbol{R})\, \Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}')\, u_j^\beta(\boldsymbol{R}') + \mathcal{O}(u^3) \quad , \tag{6.134}$$

where

$$\Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\boldsymbol{R})\, \partial u_j^\beta(\boldsymbol{R}')} \quad . \tag{6.135}$$

Remember that the indices i and j run over the set $\{1, \ldots, r\}$, where r is the number of basis vectors, while α and β are Cartesian vector indices taken from $\{1, 2, \ldots, d\}$, where d is the dimension of space.

In the case of molecules, the dynamical matrix is of rank dN. For a molecule with no point group symmetries, this is the dimension of the eigenvalue problem to be solved. In crystals, by contrast, we may take advantage of translational invariance to reduce the dimension of the eigenvalue problem to dr, *i.e.* to the number of degrees of freedom within a unit cell. This is so even in the case of a triclinic system with no symmetries (*i.e.* point group C_1). Each vibrational state is labeled by a wavevector $\boldsymbol{k}$, and at certain high symmetry points $\boldsymbol{k}$ in the Brillouin zone, crystallographic point group symmetries may be used to group these dr states into multiplets transforming according to point group IRREPs.

Upon Fourier transform,

$$\begin{aligned} u_i^\alpha(\boldsymbol{R}) &= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{u}_i^\alpha(\boldsymbol{k})\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_i} \\ p_i^\alpha(\boldsymbol{R}) &= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}} \hat{p}_i^\alpha(\boldsymbol{k})\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_i} \quad , \end{aligned} \tag{6.136}$$

where the sum is over all $\boldsymbol{k}$ within the first Brillouin zone. The Fourier space dynamical matrix is then

$$\hat{\varPhi}_{ij}^{\alpha\beta}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \varPhi_{ij}^{\alpha\beta}(\boldsymbol{R})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{\delta}_i}\, e^{i\boldsymbol{k}\cdot\boldsymbol{\delta}_j} \quad . \tag{6.137}$$

The Hamiltonian, to quadratic order, takes the form

$$H = \sum_{\boldsymbol{k},i} \frac{\hat{p}_i^\alpha(\boldsymbol{k})\, \hat{p}_i^\alpha(-\boldsymbol{k})}{2m_i} + \frac{1}{2} \sum_{\boldsymbol{k}} \sum_{i,j} \sum_{\alpha,\beta} \hat{u}_i^\alpha(-\boldsymbol{k})\, \hat{\varPhi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \hat{u}_j^\beta(\boldsymbol{k}) \quad , \tag{6.138}$$

Note that $\hat{u}_i^\alpha(-\boldsymbol{k}) = \big[\hat{u}_i^\alpha(\boldsymbol{k})\big]^*$ because the displacements $u_i^\alpha(\boldsymbol{R})$ are real; a corresponding relation holds for the momenta. Note also the Poisson bracket relation in crystal momentum space becomes

$$\Big\{ u_i^\alpha(\boldsymbol{R}) \,,\, p_j^\beta(\boldsymbol{R}') \Big\}_{\mathsf{PB}} = \delta_{\boldsymbol{R}\boldsymbol{R}'}\, \delta_{ij}\, \delta_{\alpha\beta} \quad \Rightarrow \quad \Big\{ \hat{u}_i^\alpha(\boldsymbol{k}) \,,\, \hat{p}_j^\beta(\boldsymbol{k}') \Big\}_{\mathsf{PB}} = \delta^{\mathsf{P}}_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}\, \delta_{ij}\, \delta_{\alpha\beta} \quad , \tag{6.139}$$

where $\delta^{\mathsf{P}}_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}} = \sum_{\boldsymbol{G}} \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{G}}$ requires $\boldsymbol{k}+\boldsymbol{k}'=\boldsymbol{0}$ modulo any reciprocal lattice vector. Note also that

$$\varPhi_{ij}^{\alpha\beta}(\boldsymbol{R}) = \varPhi_{ji}^{\beta\alpha}(-\boldsymbol{R}) \quad \Rightarrow \quad \hat{\varPhi}_{ji}^{\beta\alpha}(\boldsymbol{k}) = \hat{\varPhi}_{ij}^{\alpha\beta}(-\boldsymbol{k}) = \big[\hat{\varPhi}_{ij}^{\alpha\beta}(\boldsymbol{k})\big]^* \quad . \tag{6.140}$$

The system is diagonalized by writing

$$\hat{u}_i^\alpha(\boldsymbol{k}) = \sum_{\lambda=1}^{dr} \hat{\mathrm{e}}_{i\lambda}^\alpha(\boldsymbol{k})\, \hat{q}_\lambda(\boldsymbol{k}) \qquad , \qquad \hat{p}_i^\alpha(\boldsymbol{k}) = m_i \sum_{\lambda=1}^{dr} \hat{\mathrm{e}}_{i\lambda}^{\alpha *}(-\boldsymbol{k})\, \hat{\pi}_\lambda(\boldsymbol{k}) \tag{6.141}$$

where $\big\{\hat{q}_\lambda(\boldsymbol{k}), \hat{\pi}_{\lambda'}(\boldsymbol{k})\big\}_{\mathsf{PB}} = \delta_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}\, \delta_{\lambda\lambda'}$ and $S_{i\alpha,\lambda}(\boldsymbol{k}) \equiv \hat{\mathrm{e}}_{i\lambda}^\alpha(\boldsymbol{k}) \equiv m_i^{-1/2}\, U_{i\alpha,\lambda}(\boldsymbol{k})$ diagonalizes the dynamical matrix, with $U_{i\alpha,\lambda}(\boldsymbol{k})$ unitary. Thus,

$$\sum_{\beta,j} \hat{\varPhi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \hat{\mathrm{e}}_{j\lambda}^\beta(\boldsymbol{k}) = m_i\, \omega_\lambda^2(\boldsymbol{k})\, \hat{\mathrm{e}}_{i\lambda}^\alpha(\boldsymbol{k}) \tag{6.142}$$

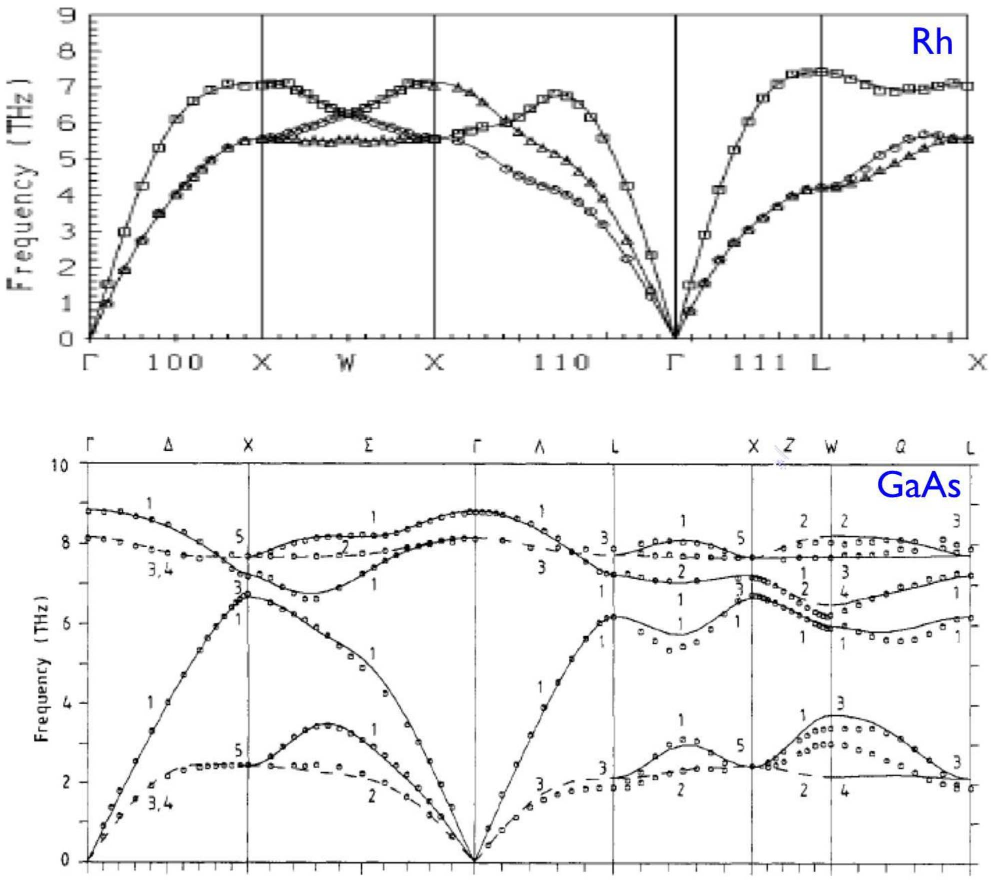

Figure 6.15: Upper panel: phonon spectrum in fcc elemental rhodium (Rh) at $T = 297\,\mathrm{K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d = 3$ and $r = 1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12\,\mathrm{K}$, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* **2**, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d = 3$ and $r = 2$. The Greek letters along the x-axis indicate points of high symmetry in the Brillouin zone.

with the completeness relation,

$$\sum_{\lambda=1}^{dr} \hat{\mathrm{e}}^{\alpha*}_{i\lambda}(\boldsymbol{k})\,\hat{\mathrm{e}}^{\beta}_{j\lambda}(\boldsymbol{k}) = \frac{1}{m_i}\,\delta_{ij}\,\delta_{\alpha\beta} \tag{6.143}$$

and the orthogonality relation,

$$\sum_{i=1}^{r}\sum_{\alpha=1}^{d} m_i\,\hat{\mathrm{e}}^{\alpha*}_{i\lambda}(\boldsymbol{k})\,\hat{\mathrm{e}}^{\alpha}_{i\lambda'}(\boldsymbol{k}) = \delta_{\lambda\lambda'} \quad , \tag{6.144}$$

which are the completeness and orthogonality relations, respectively. Since $\hat{\mathrm{e}}^{\alpha*}_{i\lambda}(-\boldsymbol{k})$ and $\hat{\mathrm{e}}^{\alpha}_{i\lambda}(\boldsymbol{k})$ obey the same equation, we have that $\omega_\lambda(-\boldsymbol{k}) = \omega_\lambda(\boldsymbol{k})$. If the phonon eigenmode $|\,\boldsymbol{k},\lambda\,\rangle$ is nondegenerate, we may choose $\hat{\mathrm{e}}^{\alpha}_{i\lambda}(-\boldsymbol{k}) = \hat{\mathrm{e}}^{\alpha*}_{i\lambda}(\boldsymbol{k})$. Else at best we can conclude $\hat{\mathrm{e}}^{\alpha}_{i\lambda}(-\boldsymbol{k}) = \hat{\mathrm{e}}^{\alpha*}_{i\lambda'}(\boldsymbol{k})\,e^{i\eta}$ where $|\,\boldsymbol{k},\lambda'\,\rangle$ is another state from the degenerate manifold of phonon states at this wavevector, and $e^{i\eta}$ is a phase.

The Hamiltonian takes the diagonalized form

$$H=\sum_{\boldsymbol{k}}\sum_{\lambda=1}^{dr}\Big\{\tfrac{1}{2}\,\hat{\pi}_\lambda(-\boldsymbol{k})\,\hat{\pi}_\lambda(\boldsymbol{k})+\tfrac{1}{2}\,\omega_\lambda^2(\boldsymbol{k})\,\hat{q}_\lambda(-\boldsymbol{k})\,\hat{q}_\lambda(\boldsymbol{k})\Big\}\quad, \tag{6.145}$$

with $\big\{\hat{q}_\lambda(\boldsymbol{k})\,,\,\hat{\pi}_{\lambda'}(\boldsymbol{k}')\big\}_{\rm PB}=\delta_{\lambda\lambda'}\,\delta^{\sf P}_{\boldsymbol{k}+\boldsymbol{k}',\boldsymbol{0}}$. To quantize, promote the Poisson brackets to commutators: $\big\{A\,,\,B\big\}_{\rm PB}\to -i\hbar^{-1}\,\big[A\,,\,B\big]$. Then define the ladder operators,

$$A_\lambda(\boldsymbol{k})=\bigg(\frac{\omega_\lambda(\boldsymbol{k})}{2\hbar}\bigg)^{1/2}\hat{q}_\lambda(\boldsymbol{k})+i\,\bigg(\frac{1}{2\hbar\omega_\lambda(\boldsymbol{k})}\bigg)^{1/2}\hat{\pi}_\lambda(\boldsymbol{k})\quad, \tag{6.146}$$

which satisfy $\big[A_\lambda(\boldsymbol{k})\,,\,A^\dagger_{\lambda'}(\boldsymbol{k}')\big]=\delta^{\sf P}_{\boldsymbol{k}\boldsymbol{k}'}\,\delta_{\lambda\lambda'}$. The quantum phonon Hamiltonian is then

$$\hat{H}=\sum_{\boldsymbol{k}}\sum_{\lambda=1}^{dr}\hbar\omega_\lambda(\boldsymbol{k})\,\Big(A^\dagger_\lambda(\boldsymbol{k})\,A_\lambda(\boldsymbol{k})+\tfrac{1}{2}\Big)\quad. \tag{6.147}$$

Of the dr phonon branches, d are *acoustic*, and behave as $\omega_a(\boldsymbol{k})=c(\hat{\boldsymbol{k}})\,k$ as $\boldsymbol{k}\to 0$, which is the Γ point in the Brillouin zone. These gapless phonons are the Goldstone bosons of the spontaneously broken translational symmetry which gave rise to the crystalline phase. To each broken generator of translation, there corresponds a Goldstone mode. The remaining $d(r-1)$ modes are called *optical phonons*. Whereas for acoustic modes, all the ions in a given unit cell are moving in phase, for optical modes they are moving out of phase. Hence optical modes are always finite frequency modes. Fig. 6.15 shows the phonon spectra in elemental rhodium (space group $Fm\overline{3}m$, point group O_h), and in gallium arsenide (space group $F\overline{4}3m$, point group T_d). Since Rh forms an fcc Bravais lattice, there are no optical phonon modes. GaAs forms a zincblende structure, *i.e.* two interpenetrating fcc lattices, one for the gallium, the other for the arsenic. Thus $r=2$ and we expect three acoustic and three optical branches of phonons.

Nota bene : One may choose to define the Fourier transforms above taking the additional phases for the basis elements to all be unity, *viz.*

$$u_i^\alpha(\boldsymbol{R})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}\hat{u}_i^\alpha(\boldsymbol{k})\,e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\quad,\quad p_i^\alpha(\boldsymbol{R})=\frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}}\hat{p}_i^\alpha(\boldsymbol{k})\,e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\quad,\quad \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})=\sum_{\boldsymbol{R}}\Phi_{ij}^{\alpha\beta}(\boldsymbol{R})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\quad. \tag{6.148}$$

All the equations starting with Eqn. 6.138 remain the same. Setting the basis phases to unity amounts to a choice of *gauge*. It is somewhat simpler in certain contexts, but it may obscure essential space group symmetries. On the other hand, it should also be noted that the Fourier transforms $\hat{u}_i^\alpha(\boldsymbol{k})$, $\hat{p}_i^\alpha(\boldsymbol{k})$, and $\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})$ are not periodic in the Brillouin zone, but instead satisfy generalized periodic boundary conditions,

$$\begin{aligned}\hat{u}_i^\alpha(\boldsymbol{K}+\boldsymbol{k})&=e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_i}\,\hat{u}_i^\alpha(\boldsymbol{k})\\ \hat{p}_i^\alpha(\boldsymbol{K}+\boldsymbol{k})&=e^{-i\boldsymbol{K}\cdot\boldsymbol{\delta}_i}\,\hat{p}_i^\alpha(\boldsymbol{k})\\ \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{K}+\boldsymbol{k})&=e^{-i\boldsymbol{K}\cdot(\boldsymbol{\delta}_i-\boldsymbol{\delta}_j)}\,\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\quad,\end{aligned} \tag{6.149}$$

where $\boldsymbol{K}\in\hat{\mathcal{L}}$ is any reciprocal lattice vector.

6.5.1 Translation and rotation invariance

The potential energy $U\big(\{u^\alpha_i(\boldsymbol{R})\}\big)$ must remain invariant under the operations

$$\begin{aligned} u^\alpha_i(\boldsymbol{R}) &\to u^\alpha_i(\boldsymbol{R}) + d^\alpha \\ u^\alpha_i(\boldsymbol{R}) &\to u^\alpha_i(\boldsymbol{R}) + \epsilon_{\alpha\mu\nu}\,(R^\mu + \delta^\mu_i - \delta^\mu_j)\, d^\nu \end{aligned} \tag{6.150}$$

for an infinitesimal vector $\boldsymbol{d}$. The first equation represents a uniform translation of all lattice sites by $\boldsymbol{d}$. The second represents an infinitesimal rotation about the $j^{\rm th}$ basis ion in the $\boldsymbol{R}=0$ unit cell. We are free to choose any j.

Writing $U(u+\Delta u) = U(u)$, we must have that the linear terms in Δu vanish, hence

$$\begin{gathered} \sum_{\boldsymbol{R},i} \varPhi^{\alpha\beta}_{ij}(\boldsymbol{R}) = \sum_i \hat{\varPhi}^{\alpha\beta}_{ij}(\boldsymbol{0}) = 0 \\ \epsilon_{\alpha\mu\nu} \sum_{\boldsymbol{R},i} (R^\mu + \delta^\mu_i - \delta^\mu_j)\, \varPhi^{\nu\beta}_{ij}(\boldsymbol{R}) = i\,\epsilon_{\alpha\mu\nu} \sum_i \frac{\partial \hat{\varPhi}^{\nu\beta}_{ij}(\boldsymbol{k})}{\partial k^\mu}\bigg|_{\boldsymbol{k}=0} = 0 \quad . \end{gathered} \tag{6.151}$$

Note that (α,β,j) are free indices in both equations. The first of these equations says that any vector d^β is an eigenvector of the dynamical matrix at $\boldsymbol{k}=0$, with zero eigenvalue. Thus, at $\boldsymbol{k}=0$, there is a three-dimensional space of zero energy modes. These are the Goldstone modes associated with the three broken generators of translation in the crystal.

6.5.2 Phonons in an fcc lattice

When the crystal is a Bravais lattice, there are no basis indices, and the dynamical matrix becomes

$$\hat{\varPhi}^{\alpha\beta}(\boldsymbol{k}) = {\sum_{\boldsymbol{R}}}' (1 - \cos \boldsymbol{k}\cdot\boldsymbol{R})\, \frac{\partial^2 v(\boldsymbol{R})}{\partial R^\alpha\, \partial R^\beta} \quad , \tag{6.152}$$

where $v(\boldsymbol{r})$ is the inter-ionic potential, and the prime on the sum indicates that $\boldsymbol{R}=0$ is to be excluded. For central potentials $v(\boldsymbol{R}) = v(R)$,

$$\frac{\partial^2 v(\boldsymbol{R})}{\partial R^\alpha\, \partial R^\beta} = \big(\delta^{\alpha\beta} - \hat{R}^\alpha\, \hat{R}^\beta\big)\, \frac{v'(R)}{R} + \hat{R}^\alpha\, \hat{R}^\beta\, v''(R) \quad . \tag{6.153}$$

For simplicity, we assume $v(R)$ is negligible beyond the first neighbor. On the fcc lattice, there are twelve first neighbors, lying at $\boldsymbol{\varDelta} = \frac{1}{2}a\,(\pm\hat{\boldsymbol{y}} \pm \hat{\boldsymbol{z}})$, $\boldsymbol{\varDelta} = \frac{1}{2}a\,(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{z}})$, and $\boldsymbol{\varDelta} = \frac{1}{2}a\,(\pm\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}})$. Here a is the side length of the underlying simple cubic lattice, so the fcc lattice constant is $a/\sqrt{2}$. We define

$$A = \frac{\sqrt{2}}{a}\, v'\big(a/\sqrt{2}\big) \quad , \quad B = v''\big(a/\sqrt{2}\big) \quad . \tag{6.154}$$

Along (100), we have $\boldsymbol{k} = k\hat{\boldsymbol{x}}$ and

$$\hat{\varPhi}^{\alpha\beta}(\boldsymbol{k}) = 4\sin^2(\tfrac{1}{4}ka) \begin{pmatrix} 2A+2B & 0 & 0 \\ 0 & 3A+B & 0 \\ 0 & 0 & 3A+B \end{pmatrix} \quad , \tag{6.155}$$

which is already diagonal. Thus, the eigenvectors lie along the cubic axes and

$$\omega_{\rm L} = 2\sqrt{\tfrac{2(A+B)}{m}}\,\big|\sin(ka/4)\big| \qquad , \qquad \omega_{\rm T1} = \omega_{\rm T2} = 2\sqrt{\tfrac{3A+B}{m}}\,\big|\sin(ka/4)\big| \quad . \tag{6.156}$$

Along (111), we have $\boldsymbol{k} = \frac{1}{\sqrt{3}}\,k\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$. One finds

$$\hat{\varPhi}^{\alpha\beta}(\boldsymbol{k}) = 4\sin^2\!\big(ka/\sqrt{12}\big) \begin{pmatrix} 4A+2B & B-A & B-A \\ B-A & 4A+2B & B-A \\ B-A & B-A & 4A+2B \end{pmatrix} \quad . \tag{6.157}$$

$$\omega_{\rm L} = 2\sqrt{\tfrac{A+2B}{m}}\,\big|\sin\!\big(ka/\sqrt{12}\big)\big| \qquad , \qquad \omega_{\rm T1} = \omega_{\rm T2} = 2\sqrt{\tfrac{5A+B}{2m}}\,\big|\sin\!\big(ka/\sqrt{12}\big)\big| \quad . \tag{6.158}$$

6.5.3 Elasticity theory redux : Bravais lattices

In a Bravais lattice, we have $\hat{\varPhi}^{\alpha\beta}(\boldsymbol{0}) = 0$ from translational invariance. The potential energy may then be written in the form

$$U = U_0 - \frac{1}{4}\sum_{\boldsymbol{R},\boldsymbol{R}'}\sum_{\alpha,\beta}\big[u^\alpha(\boldsymbol{R}) - u^\alpha(\boldsymbol{R}')\big]\,\varPhi^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}')\,\big[u^\beta(\boldsymbol{R}) - u^\beta(\boldsymbol{R}')\big] \quad . \tag{6.159}$$

We now assume a very long wavelength disturbance, and write

$$u^\alpha(\boldsymbol{R}) - u^\alpha(\boldsymbol{R}') = (R^\mu - R'^\mu)\,\frac{\partial u^\alpha}{\partial x^\mu}\bigg|_{\boldsymbol{R}} + \ldots \quad . \tag{6.160}$$

Thus,

$$U = U_0 - \frac{1}{4}\sum_{\boldsymbol{R},\boldsymbol{R}'}\sum_{\alpha,\beta}\sum_{\mu,\nu}\frac{\partial u^\alpha}{\partial x^\mu}\bigg|_{\boldsymbol{R}}\,\frac{\partial u^\beta}{\partial x^\nu}\bigg|_{\boldsymbol{R}}\,(R^\mu - R'^\mu)\,(R^\nu - R'^\nu)\,\varPhi^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}') \quad . \tag{6.161}$$

We may symmetrize with respect to Cartesian indices[38] to obtain the elastic tensor

$$C_{\alpha\beta\mu\nu} \equiv -\frac{1}{8\varOmega}\sum_{\boldsymbol{R}}\Big(R^\mu R^\nu\,\varPhi^{\alpha\beta}(\boldsymbol{R}) + R^\mu R^\beta\,\varPhi^{\alpha\nu}(\boldsymbol{R}) + R^\alpha R^\nu\,\varPhi^{\mu\beta}(\boldsymbol{R}) + R^\alpha R^\beta\,\varPhi^{\mu\nu}(\boldsymbol{R})\Big) \quad . \tag{6.162}$$

Note that

$$C_{\alpha\beta\mu\nu} = C_{\beta\alpha\mu\nu} = C_{\alpha\beta\nu\mu} = C_{\mu\nu\alpha\beta} \quad , \tag{6.163}$$

where $\varOmega$ is the Wigner-Seitz cell volume.

Elasticity in solids

Recall from §6.3.6 that we may regard the rank four tensor $C_{\alpha\beta\mu\nu}$ as a symmetric 6×6 matrix C_{ab}, where we replace $(\alpha\beta)\to a$ and $(\mu\nu)\to b$ according to the scheme which we repeat from Tab. 6.15: In cubic

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[38] Symmetrization is valid because the antisymmetric combination $\big(\frac{\partial u^\alpha}{\partial x^\beta} - \frac{\partial u^\beta}{\partial x^\alpha}\big)$ corresponds to a rotation.

$(\alpha\beta):$	(11)	(22)	(33)	(23)	(31)	(12)
$a:$	1	2	3	4	5	6

Table 6.20: Abbreviation for symmetric compound indices $(\alpha\beta)$.

crystals, for example, we have

$$\begin{aligned} C_{11} &= C_{xxxx} = C_{yyyy} = C_{zzzz} \\ C_{12} &= C_{xxyy} = C_{xxzz} = C_{yyzz} \\ C_{44} &= C_{xyxy} = C_{xzxz} = C_{yzyz} \quad . \end{aligned} \tag{6.164}$$

Typical values of C_{ab} in solids are on the order of gigapascals, *i.e.* 10^9 Pa:

element	C_{11}	C_{12}	C_{44}
^{4}He	0.031	0.028	0.022
Cu	16	8	12
Al	108	62	28.3
Pb	48.8	41.4	14.8
C (diamond)	1040	170	550

Table 6.21: Elastic moduli for various solids (in GPa).

The *bulk modulus* of a solid is defined as $\mathcal{B} = V\,\partial^2 F/\partial V^2$. We consider a uniform dilation, which is described by $\boldsymbol{R} \to (1+\zeta)\boldsymbol{R}$ at each lattice site. Thus the displacement field is $\boldsymbol{u}(\boldsymbol{r}) = \zeta\boldsymbol{r}$. This leads to a volume change of $\delta V = 3\zeta V$, hence $\zeta = \delta V/3V$. The strain tensor is $\varepsilon_{\alpha\beta} = \zeta\,\delta_{\alpha\beta}$, hence

$$\delta F = \frac{(\delta V)^2}{18V} \sum_{\alpha,\beta} C_{\alpha\alpha\beta\beta} = \tfrac{1}{9} \sum_{a,b=1}^{3} C_{ab} \quad . \tag{6.165}$$

Thus, for cubic materials, $\mathcal{B} = \frac{1}{3}C_{11} + \frac{2}{3}C_{12}$.

Elastic waves

The Lagrangian of an elastic medium is be written as

$$L = \int\! d^d\!r\, \mathcal{L} = \int\! d^d\!r \left\{ \tfrac{1}{2}\,\rho \left(\frac{\partial u^\alpha}{\partial t}\right)^2 - \tfrac{1}{2}\,C_{\alpha\beta\mu\nu}\,\frac{\partial u^\alpha}{\partial x^\beta}\,\frac{\partial u^\mu}{\partial x^\nu} \right\} \quad , \tag{6.166}$$

where ρ is the overall mass density of the crystal, *i.e.* $\rho = m/\Omega$. The Euler-Lagrange equations of motion are then

$$\begin{aligned} 0 &= \frac{\partial}{\partial t}\,\frac{\partial\mathcal{L}}{\partial(\partial_t u^\alpha)} + \frac{\partial}{\partial x^\beta}\,\frac{\partial\mathcal{L}}{\partial(\partial_\beta u^\alpha)} \\ &= \rho\,\frac{\partial^2 u^\alpha}{\partial t^2} - C_{\alpha\beta\mu\nu}\,\frac{\partial^2 u^\nu}{\partial x^\beta\,\partial x^\mu} \quad . \end{aligned} \tag{6.167}$$

The solutions are *elastic waves*, with $\boldsymbol{u}(\boldsymbol{x},t) = \hat{\mathrm{e}}(\boldsymbol{k})\,e^{i(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)}$ where

$$\rho\omega^2\,\mathrm{e}^\alpha(\boldsymbol{k}) = C_{\alpha\beta\mu\nu}\,k^\beta\,k^\mu\,\mathrm{e}^\nu(\boldsymbol{k}) \quad . \tag{6.168}$$

Thus, the dispersion is $\omega_a(\boldsymbol{k}) = c_a(\hat{\boldsymbol{k}})\,k$, where

$$\det\Big[\rho\,c^2(\hat{\boldsymbol{k}})\,\delta_{\alpha\nu} - C_{\alpha\beta\mu\nu}\,\hat{k}^\beta\,\hat{k}^\mu\Big] = 0 \tag{6.169}$$

is the equation to be solved for the speeds of sound $c_a(\hat{\boldsymbol{k}})$ in each elastic wave branch a.

For isotropic solids, $C_{12} \equiv \lambda$, $C_{44} \equiv \mu$, and $C_{11} = C_{12} + 2C_{14} = \lambda + 2\mu$, where λ and μ are the Lamé coefficients. The free energy density is discussed in §6.3.6 and is given by

$$f = \tfrac{1}{2}\lambda\,(\partial_i u_i)^2 + \tfrac{1}{2}\mu\,(\partial_i u_j)\,(\partial_i u_j) + \tfrac{1}{2}\mu\,(\partial_i u_j)\,(\partial_j u_i) \quad , \tag{6.170}$$

which results in the Euler-Lagrange equations of motion

$$\rho\,\ddot{\boldsymbol{u}} = (\lambda+\mu)\,\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{u}) + \mu\,\nabla^2\boldsymbol{u} \quad . \tag{6.171}$$

Writing $\boldsymbol{u}(\boldsymbol{r},t) = u_0\,\hat{\mathrm{e}}(\boldsymbol{k})\,e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$, where $\hat{\mathrm{e}}$ is a polarization unit vector, we obtain a longitudinal mode when $\hat{\mathrm{e}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}} = 1$ with $\omega_{\mathsf{L}}(\boldsymbol{k}) = c_{\mathsf{L}}\,|\boldsymbol{k}|$ and $c_{\mathsf{L}} = \sqrt{(\lambda+2\mu)/\rho}$, and two transverse modes when $\hat{\mathrm{e}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}} = 0$ with $\omega_{\mathsf{T}}(\boldsymbol{k}) = c_{\mathsf{T}}\,|\boldsymbol{k}|$ and $c_{\mathsf{T}} = \sqrt{\mu/\rho}$.

In cubic crystals, there are three independent elastic moduli, C_{11}, C_{12}, and C_{14}. We then have

$$\begin{aligned} \rho\,c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^x &= \Big[C_{11}\,\hat{k}_x^2 + C_{44}\big(\hat{k}_y^2 + \hat{k}_z^2\big)\Big]\hat{\mathrm{e}}^x + (C_{12}+C_{44})\big(\hat{k}_x\,\hat{k}_y\,\hat{\mathrm{e}}^y + \hat{k}_x\,\hat{k}_z\,\hat{\mathrm{e}}^z\big) \\ \rho\,c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^y &= \Big[C_{11}\,\hat{k}_y^2 + C_{44}\big(\hat{k}_x^2 + \hat{k}_z^2\big)\Big]\hat{\mathrm{e}}^y + (C_{12}+C_{44})\big(\hat{k}_x\,\hat{k}_y\,\hat{\mathrm{e}}^x + \hat{k}_y\,\hat{k}_z\,\hat{\mathrm{e}}^z\big) \\ \rho\,c^2(\hat{\boldsymbol{k}})\,\mathrm{e}^z &= \Big[C_{11}\,\hat{k}_z^2 + C_{44}\big(\hat{k}_x^2 + \hat{k}_y^2\big)\Big]\hat{\mathrm{e}}^z + (C_{12}+C_{44})\big(\hat{k}_x\,\hat{k}_z\,\hat{\mathrm{e}}^x + \hat{k}_y\,\hat{k}_z\,\hat{\mathrm{e}}^y\big) \quad . \end{aligned} \tag{6.172}$$

This still yields a cubic equation, but it can be simplified by looking along a high symmetry direction in the Brillouin zone.

Along the (100) direction $\boldsymbol{k} = k\,\hat{\boldsymbol{x}}$, we have

$$\hat{\mathbf{e}}_{\mathrm{L}} = \hat{\boldsymbol{x}} \qquad\qquad c_{\mathrm{L}} = \sqrt{C_{11}/\rho} \tag{6.173}$$

$$\hat{\mathbf{e}}_{\mathrm{T1}} = \hat{\boldsymbol{y}} \qquad\qquad c_{\mathrm{T1}} = \sqrt{C_{44}/\rho} \tag{6.174}$$

$$\hat{\mathbf{e}}_{\mathrm{T2}} = \hat{\boldsymbol{z}} \qquad\qquad c_{\mathrm{T2}} = \sqrt{C_{44}/\rho} \quad . \tag{6.175}$$

Along the (110) direction, we have $\boldsymbol{k} = \frac{1}{\sqrt{2}}\,k\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})$. In this case

$$\hat{\mathbf{e}}_{\mathrm{L}} = \tfrac{1}{\sqrt{2}}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) \qquad c_{\mathrm{L}} = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho} \tag{6.176}$$

$$\hat{\mathbf{e}}_{\mathrm{T1}} = \tfrac{1}{\sqrt{2}}(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}}) \qquad c_{\mathrm{T1}} = \sqrt{(C_{11} - C_{12})/2\rho} \tag{6.177}$$

$$\hat{\mathbf{e}}_{\mathrm{T2}} = \hat{\boldsymbol{z}} \qquad c_{\mathrm{T2}} = \sqrt{C_{44}/\rho} \quad . \tag{6.178}$$

Along the (111) direction, we have $\boldsymbol{k} = \frac{1}{\sqrt{3}}\,k\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$. In this case

$$\hat{\mathbf{e}}_{\mathrm{L}} = \tfrac{1}{\sqrt{3}}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) \qquad c_{\mathrm{L}} = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho} \tag{6.179}$$

$$\hat{\mathbf{e}}_{\mathrm{T1}} = \tfrac{1}{\sqrt{6}}(2\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}) \qquad c_{\mathrm{T1}} = \sqrt{(C_{11} - C_{12})/3\rho} \tag{6.180}$$

$$\hat{\mathbf{e}}_{\mathrm{T2}} = \tfrac{1}{\sqrt{2}}(\hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}) \qquad c_{\mathrm{T2}} = \sqrt{(C_{11} - C_{12})/3\rho} \quad . \tag{6.181}$$

6.5.4 Elasticity theory in cases with bases

The derivation of the elastic tensor $C_{\alpha\beta\mu\nu}$ is significantly complicated by the presence of a basis. Sadly, translational invariance if of no direct avail because

$$U \neq U_0 - \frac{1}{4} \sum_{\boldsymbol{R},\boldsymbol{R}'} \sum_{\alpha,\beta} \sum_{i,j} \big[u_i^\alpha(\boldsymbol{R}) - u_i^\alpha(\boldsymbol{R}')\big]\, \Phi_{ij}^{\alpha\beta}(\boldsymbol{R} - \boldsymbol{R}')\, \big[u_j^\beta(\boldsymbol{R}) - u_j^\beta(\boldsymbol{R}')\big] \quad . \tag{6.182}$$

The student should understand why the above relation is not an equality.

Rather than work with the energy, we will work with the eigenvalue equation 6.142,

$$\hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \hat{\mathrm{e}}_{j\lambda}^{\beta}(\boldsymbol{k}) = m_i\, \omega_\lambda^2(\boldsymbol{k})\, \hat{\mathrm{e}}_{i\lambda}^{\alpha}(\boldsymbol{k}) \quad ,$$

and expand in powers of $\boldsymbol{k}$. Accordingly, we write

$$\begin{aligned} \hat{\mathrm{e}}_{i\lambda}^{\alpha}(\boldsymbol{k}) &= d_i^\alpha + k^\sigma f_{i\sigma}^\alpha + \tfrac{1}{2}\, k^\sigma k^\tau g_{i\sigma\tau}^\beta + \mathcal{O}(k^3) \\ \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k}) &= \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) + k^\mu\, \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu}\bigg|_{\boldsymbol{0}} + \tfrac{1}{2}\, k^\mu\, k^\nu\, \frac{\partial^2 \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu\, \partial k^\nu}\bigg|_{\boldsymbol{0}} + \mathcal{O}(k^3) \quad . \end{aligned} \tag{6.183}$$

We retain the basis index i on d_i^α *even though it is independent of* i because we will use it to make clear certain necessary sums on the basis index within the Einstein convention. We then have

$$\begin{aligned} & m_i\, \omega^2 \Big\{ d_i^\alpha + k^\sigma f_{i\sigma}^\alpha + \ldots \Big\} = \\ & \qquad \left\{ \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{0}) + k^\mu\, \frac{\partial \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu}\bigg|_{\boldsymbol{0}} + \tfrac{1}{2}\, k^\mu\, k^\nu\, \frac{\partial^2 \hat{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})}{\partial k^\mu\, \partial k^\nu}\bigg|_{\boldsymbol{0}} + \ldots \right\} \Big\{ d_j^\beta + k^\tau f_{j\tau}^\beta + \ldots \Big\} \quad , \end{aligned} \tag{6.184}$$

where there is no implied sum on i on the LHS. We now work order by order in $\boldsymbol{k}$. To start, note that $\omega^2(\boldsymbol{k}) = c^2(\hat{\boldsymbol{k}})\,k^2$ is already second order. On the RHS, we have $\hat{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{0})\,d^\beta_j = 0$ to zeroth order in k. At first order, we must have

$$\hat{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{0})\,f^\beta_{j\sigma} + \frac{\partial\hat{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{k})}{\partial k^\sigma}\bigg|_{\boldsymbol{0}} d^\beta_j = 0 \quad , \tag{6.185}$$

and defining the matrix inverse $\hat{\Upsilon}^{\gamma\alpha}_{li}(\boldsymbol{k})$ by the relation

$$\hat{\Upsilon}^{\gamma\alpha}_{li}(\boldsymbol{k})\,\hat{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{k}) = \delta^{\gamma\beta}\,\delta_{lj} \quad , \tag{6.186}$$

we have

$$f^\gamma_{l\sigma} = -\hat{\Upsilon}^{\gamma\alpha}_{li}(\boldsymbol{0})\,\frac{\partial\hat{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{k})}{\partial k^\sigma}\bigg|_{\boldsymbol{0}} d^\beta_j \tag{6.187}$$

Finally, we obtain the eigenvalue equation for the elastic waves,

$$m_i\,\omega^2\,d^\alpha_i = \left[\frac{1}{2}\,\frac{\partial^2\hat{\Phi}^{\alpha\beta}_{il}(\boldsymbol{k})}{\partial k^\mu\,\partial k^\nu}\bigg|_{\boldsymbol{0}} - \frac{\partial\hat{\Phi}^{\alpha\sigma}_{ij}(\boldsymbol{k})}{\partial k^\mu}\bigg|_{\boldsymbol{0}}\,\hat{\Upsilon}^{\sigma\gamma}_{jm}(\boldsymbol{0})\,\frac{\partial\hat{\Phi}^{\gamma\beta}_{ml}(\boldsymbol{k})}{\partial k^\nu}\bigg|_{\boldsymbol{0}}\right] k^\mu\,k^\nu\,d^\beta_l \quad . \tag{6.188}$$

Remember that d^α_i is independent of the basis index i. We have dropped the mode index λ here for notational convenience. Note that the quadratic coefficient $g^\beta_{i\sigma\tau}$ never entered our calculation because it leads to an inhomogeneous term in the eigenvalue equation, and therefore must be dropped. We do not report here the explicit form for the elastic tensor, which may be derived from the above eigenvalue equation.

6.6 Appendix : $\mathbf{O}(3)$ Characters of Point Group Operations

In tables Tab. 6.22 and 6.23 we present the characters of all crystallographic point group operations for several integer and half-odd-integer representations of SO(3).

6.7 Appendix : Construction of Group Invariants

6.7.1 Polar and axial vectors

We follow the discussion in §4.5 of Lax. Let $\boldsymbol{r}_j$ denote a polar vector and $\boldsymbol{m}_k$ an axial vector, where j and k are labels. Let's first recall how axial vectors transform. If we write $m_\mu = \epsilon_{\mu\nu\lambda}\,r^\nu_1\,r^\lambda_2$, where $\boldsymbol{r}_{1,2}$ are polar vectors, then under the action of a group element g, we have $\boldsymbol{m} \to \boldsymbol{m}'$, where

$$m'_\mu = \epsilon_{\mu\nu\lambda}\,D_{\nu'\nu}(g)\,D_{\lambda'\lambda}(g)\,r^{\nu'}_1\,r^{\lambda'}_2 \quad . \tag{6.189}$$

Now if R is any 3×3 matrix, then $R_{\mu'\mu}\,R_{\nu'\nu}\,R_{\lambda'\lambda}\,\epsilon^{\mu\nu\lambda} = \det(R)\,\epsilon^{\mu'\nu'\lambda'}$, and therefore $m'_\mu = m_{\mu'}\,\widetilde{D}_{\mu'\mu}(g)$, where $\widetilde{D}_{\alpha\beta}(g) = \det D(g)\cdot D_{\alpha\beta}(g)$. In other words,

$$\epsilon_{\mu\nu\lambda}\,D_{\nu'\nu}(g)\,D_{\lambda'\lambda}(g) = \det D(g)\cdot\epsilon_{\mu'\nu'\lambda'}D_{\mu'\mu}(g) \quad . \tag{6.190}$$

J	E	C_2	C_3	C_4	C_6	$\overline{E}$	$\overline{C}_3$	$\overline{C}_4$	$\overline{C}_6$
$1/2$	2	0	1	$\sqrt{2}$	$\sqrt{3}$	-2	-1	$-\sqrt{2}$	$-\sqrt{3}$
1	3	-1	0	1	2	3	0	1	2
$3/2$	4	0	-1	0	$\sqrt{3}$	-4	1	0	$-\sqrt{3}$
2	5	1	-1	-1	1	5	-1	-1	1
$5/2$	6	0	0	$-\sqrt{2}$	0	-6	0	$\sqrt{2}$	0
3	7	-1	1	-1	-1	7	1	-1	-1
$7/2$	8	0	1	0	$-\sqrt{3}$	-8	-1	0	$\sqrt{3}$
4	9	1	0	1	-2	9	0	1	-2
$9/2$	10	0	-1	$\sqrt{2}$	$-\sqrt{3}$	-10	1	$-\sqrt{2}$	$\sqrt{3}$
5	11	-1	-1	1	-1	11	-1	1	-1
$11/2$	12	0	0	0	0	-12	0	0	0
6	13	1	1	-1	1	13	1	-1	1

Table 6.22: $\mathsf{O}(3)$ characters of crystallographic point group operations. Note $\chi(\overline{C}_2) = \chi(C_2)$.

$\chi(\sigma)$	$\chi(\overline{\sigma})$	$\chi(I)$	$\chi(\overline{I})$	$\chi(S_3)$	$\chi(S_4)$	$\chi(S_6)$	$\chi(\overline{S}_3)$	$\chi(\overline{S}_4)$	$\chi(\overline{S}_6)$
$\eta\,\chi(C_2)$	$\eta\,\chi(C_2)$	$\eta\,\chi(E)$	$\eta\,\chi(\overline{E})$	$\eta\,\chi(C_6)$	$\eta\,\chi(C_4)$	$\eta\,\chi(C_3)$	$\eta\,\chi(\overline{C}_6)$	$\eta\,\chi(\overline{C}_4)$	$\eta\,\chi(\overline{C}_3)$

Table 6.23: Characters for improper $\mathsf{O}(3)$ operations. Here $\eta = \pm$ is the parity.

Thus for proper rotations, $\boldsymbol{m}$ transforms in the same way as a polar vector. But for improper operations, it incurs an extra minus sign. From these results, we can also determine that

- For polar vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, the cross product $\boldsymbol{r}_1 \times \boldsymbol{r}_2$ transforms as an axial vector (proven above).
- For axial vectors $\boldsymbol{m}_1$ and $\boldsymbol{m}_2$, the cross product $\boldsymbol{m}_1 \times \boldsymbol{m}_2$ also transforms as an axial vector.
- The cross product $\boldsymbol{r} \times \boldsymbol{m}$ of a polar vector with an axial vector transforms as a polar vector.

6.7.2 Invariant tensors

Suppose $T_{\alpha_1 \cdots \alpha_N \mu_1 \cdots \mu_M}$ transforms as a polar vector (*i.e.* 1^-) with respect to the indices $\{\alpha_j\}$ and as an axial vector (*i.e.* 1^+) with respect to indices $\{\mu_k\}$. Then the function

$$T\big(\{\boldsymbol{r}_j\}, \{\boldsymbol{m}_k\}\big) = T_{\alpha_1 \cdots \alpha_N \mu_1 \cdots \mu_M} \prod_{j=1}^{N} r_j^{\alpha_j} \prod_{k=1}^{M} m_k^{\mu_k} \quad . \tag{6.191}$$

transforms as a scalar (*i.e.* the trivial representation) under $\mathsf{O}(3)$. For example, if $T_{\alpha\beta\mu}$ transforms as a (polar) vector under α and β, and as an (axial) pseudovector under μ, then $T(\boldsymbol{x},\boldsymbol{y},\boldsymbol{m}) = T_{\alpha\beta\mu}\,x^\alpha\,y^\beta\,m^\mu$ is an invariant if $\boldsymbol{x}$ and $\boldsymbol{y}$ are vectors and $\boldsymbol{m}$ a pseudovector. Basically, so long as one is always taking the "dot product" on indices transforming according to the same IRREP of $\mathsf{O}(3)$, either 1^- or 1^+, then the resulting expression is a group scalar if all available indices are contracted. This also holds true if one internally contracts tensor indices which transform in the same way, *e.g.*

$$\widetilde{T}\big(\{\boldsymbol{r}_j\},\{\boldsymbol{m}_k\}\big) = T_{\alpha_1\cdots\alpha_N\mu_1\cdots\mu_M}\,\delta^{\alpha_1\alpha_2}\,\delta^{\mu_1\mu_2}\,\delta^{\mu_3\mu_4}\prod_{j=3}^{N} r_j^{\alpha_j}\prod_{k=5}^{M} m_k^{\mu_k} \tag{6.192}$$

is also a scalar. Now, following Lax, to every invariant polynomial of homogeneous degree K in $\big(\{\boldsymbol{r}_j\,,\,\boldsymbol{m}_k\}\big)$ there corresponds an invariant tensor of rank K, which one reads off from the coefficients of the monomials. Recall that any polynomial for which

$$T(\lambda\boldsymbol{r}_1,\ldots,\lambda\boldsymbol{r}_N,\lambda\boldsymbol{m}_1,\ldots,\lambda\boldsymbol{m}_M) = \lambda^K\,T(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{m}_1,\ldots,\boldsymbol{m}_M) \tag{6.193}$$

is homogeneous of degree K. Thus, $T(\boldsymbol{x},\boldsymbol{y},\boldsymbol{m}) = \boldsymbol{x}\times\boldsymbol{y}\cdot\boldsymbol{m} = \epsilon_{\alpha\beta\gamma}\,x^\alpha\,y^\beta\,m^\mu$ is invariant and homogeneous of degree $K=3$. Therefore $T_{\alpha\beta\mu} = c\,\epsilon_{\alpha\beta\mu}$, where c is any constant, is an invariant rank three tensor, inverting the logic of our previous example.

For the group $\mathsf{SO}(n)$ of proper rotations, a theorem which we shall not prove establishes that all polynomial invariants of the n vectors $\{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n\}$ are of the form

$$P(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n) = P_1\big(\{\boldsymbol{r}_i\cdot\boldsymbol{r}_j\}\big) + P_2\big(\{\boldsymbol{r}_i\cdot\boldsymbol{r}_j\}\big)\,\mathsf{det}(r_i^\mu) \quad , \tag{6.194}$$

where $P_{1,2}$ are functions of the dot products $\boldsymbol{r}_i\cdot\boldsymbol{r}_j$. In fact, the determinant is also a function of the dot products, although not a polynomial function thereof: $\mathsf{det}\,M_{i\mu} \equiv \mathsf{det}(r_i^\mu) = \mathsf{det}^{1/2}(\boldsymbol{r}_i\cdot\boldsymbol{r}_j) \equiv \big(\mathsf{det}\,N_{ij}\big)^{1/2}$.

6.7.3 Shell theorem

Let $\big\{\phi^\Gamma_\mu(\boldsymbol{r})\big\}$ and $\big\{\psi^\Gamma_\nu(\boldsymbol{r})\big\}$ be two sets of orthonormal basis functions for an IRREP Γ of some finite discrete group G. Then the function

$$F^\Gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_{\mu=1}^{d_\Gamma}\phi^{\Gamma*}_\mu(\boldsymbol{r})\,\psi^\Gamma_\mu(\boldsymbol{r}') \tag{6.195}$$

is invariant under the operation of all $g\in G$. Explicitly, we have

$$g\,F^\Gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_{\alpha,\beta}\phi^{\Gamma*}_\alpha(\boldsymbol{r})\,\psi^\Gamma_\beta(\boldsymbol{r}')\,\overbrace{\sum_\mu D^*_{\alpha\mu}(g)\,D_{\beta\mu}(g)}^{=\,\delta_{\alpha\beta}} \quad . \tag{6.196}$$

Similarly, we have

$$\frac{1}{N_G}\sum_{g\in G} g\,\Big[\phi^{\Gamma*}_\mu(\boldsymbol{r})\,\psi^\Gamma_\mu(\boldsymbol{r}')\Big] = \sum_{\alpha,\beta}\phi^{\Gamma*}_\alpha(\boldsymbol{r})\,\psi^\Gamma_\beta(\boldsymbol{r}')\,\frac{1}{N_G}\sum_{g\in G}D^*_{\alpha\mu}(g)\,D_{\beta\mu}(g) = \frac{1}{d_\Gamma}\sum_\alpha\phi^{\Gamma*}_\alpha(\boldsymbol{r})\,\psi^\Gamma_\alpha(\boldsymbol{r}') \quad , \tag{6.197}$$

where there is no implicit sum on μ. The LHS above is an average over all group operations, whereas the RHS is a "shell average" over all the labels in the representation Γ.

These results may be used to construct invariant tensors. Lax presents an example from C_{3v}, taking

$$\phi^E_1 = yz' - zy' \quad , \quad \phi^E_2 = zx' - xz' \quad , \quad \psi^E_1 = m_x \quad , \quad \psi^E_2 = m_y \quad , \tag{6.198}$$

and

$$\phi^{A_2} = xy' - yx' \quad , \quad \psi^{A_2} = m_z \quad . \tag{6.199}$$

The general invariant is expressed as $F = a\,E\!\cdot\! E + b\,A_2\!\cdot\! A_2$, *i.e.*

$$F = a\,(yz' - zy')\,m_x + a\,(zx' - xz')\,m_y + b\,(xy' - yx')\,m_z \quad . \tag{6.200}$$

We read off the coefficients of $r_\mu\, r'_\nu\, m_\lambda$ to obtain the invariant tensor elements $\chi_{\mu\nu\lambda}$,

$$\begin{aligned} \chi_{123} = -\chi_{213} &= a \\ \chi_{231} = \chi_{312} = -\chi_{321} = -\chi_{132} &= b \quad . \end{aligned} \tag{6.201}$$

With spin, the invariant carries spatial and spin information, and is written

$$F^\Gamma(\boldsymbol{r},\boldsymbol{r}',s,s') = \sum_{\mu=1}^{d_\Gamma} \phi^{\Gamma*}_\mu(\boldsymbol{r},s)\,\psi^\Gamma_\mu(\boldsymbol{r}',s') \quad , \tag{6.202}$$

where s and s' are spinor indices.

6.8 Appendix : Quasi-degenerate Perturbation Theory

Oftentimes, as in our discussion of Raman spectroscopy in §6.4.3, we would like to focus on a subset of Hilbert space and derive an effective Hamiltonian valid for a restricted group of states. This may be accomplished by decoupling the target group of states from the rest of Hilbert space perturbatively order by order in a canonical transformation[39].

6.8.1 Type A and type B operators

Consider a Hamiltonian $H = H^0 + V$, with $H^0 |\, j\,\rangle = E^0_j |\, j\,\rangle$. Typically the Hilbert space in which H operates will be infinite-dimensional. Now consider some finite subset of levels $\{j_1, j_j, \ldots, j_K\}$ and define P to be be the projector onto this subspace, *i.e.* $P = \sum_{\alpha=1}^K |\, j_\alpha \rangle\langle j_\alpha\,|$. Let $Q = \mathbb{1} - P$ be the orthogonal projector onto the complementary subspace. Typically we will be interested in cases where P projects onto a small number of energy levels, such as the low-lying vibrational states of a molecule, or, in a solid, a group of levels in the vicinity of the Fermi energy, such as the valence band(s) plus conduction band(s) in a semiconductor.

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[39] See, *e.g.* Appendix B of R. Winkler, *Spin-Orbit Coupling Effects in Two-Dimensional Electron and Hole Systems* (Springer, 2003).

Let us write $V = V_\mathrm{A} + V_\mathrm{B}$, where

$$\begin{aligned} V_\mathrm{A} &= PVP + QVQ \\ V_\mathrm{B} &= PVQ + QVP \quad . \end{aligned} \tag{6.203}$$

The operator V_A has no matrix elements connecting the P and Q subspaces, while V_B *only* has matrix elements between those subspaces. Clearly H^0, which is diagonal, is a "type A" operator. Fig. 6.16 shows schematically the difference between type A and type B.

6.8.2 Unitary transformation for block diagonalization

Consider now a unitary transformation with

$$\begin{aligned} \widetilde{H} = e^{-S}\,H\,e^{S} &= H + [H,S] + \frac{1}{2!}\big[[H,S],S\big] + \frac{1}{3!}\Big[\big[[H,S],S\big],S\Big] + \ldots \\ &\equiv \sum_{k=0}^{\infty} \frac{1}{k!}\,\big[H,S\big]_{(k)} \ , \end{aligned} \tag{6.204}$$

where $S = -S^\dagger$ is antihermitian in order that e^S be unitary, and where

$$\big[H,S\big]_{(k)} = \overbrace{\big[\big[\big[H,S\big],S\big]\cdots,S\big]}^{k \text{ times}} \ , \tag{6.205}$$

with $[H,S]_{(0)} \equiv H$. As we shall see, we may assume $S = S_\mathrm{B}$ is of type B., in which case $\widetilde{H} = \widetilde{H}_\mathrm{A} + \widetilde{H}_\mathrm{B}$, with

$$\begin{aligned} \widetilde{H}_\mathrm{A} &= \sum_{j=0}^{\infty} \frac{1}{(2j)!}\big[H^0 + V_\mathrm{A}, S\big]_{(2j)} + \sum_{j=0}^{\infty} \frac{1}{(2j+1)!}\big[V_\mathrm{B}, S\big]_{(2j+1)} \\ \widetilde{H}_\mathrm{B} &= \sum_{j=0}^{\infty} \frac{1}{(2j+1)!}\big[H^0 + V_\mathrm{A}, S\big]_{(2j+1)} + \sum_{j=0}^{\infty} \frac{1}{(2j)!}\big[V_\mathrm{B}, S\big]_{(2j)} \quad . \end{aligned} \tag{6.206}$$

We choose S such that $\widetilde{H}_\mathrm{B} = 0$. This is done perturbatively. We start by formally replacing $V_\mathrm{A} \to \lambda V_\mathrm{A}$ and $V_\mathrm{B} \to \lambda V_\mathrm{B}$, with $\lambda = 1$ at the end of the day. We then write S as a Taylor series in powers of λ:

$$S = \lambda\, S^{(1)} + \lambda^2\, S^{(2)} + \ldots \quad . \tag{6.207}$$

X	Y	$[X,Y]$
type A	type A	type A
type A	type B	type B
type B	type A	type B
type B	type B	type A

Table 6.24: Commutators and their types.

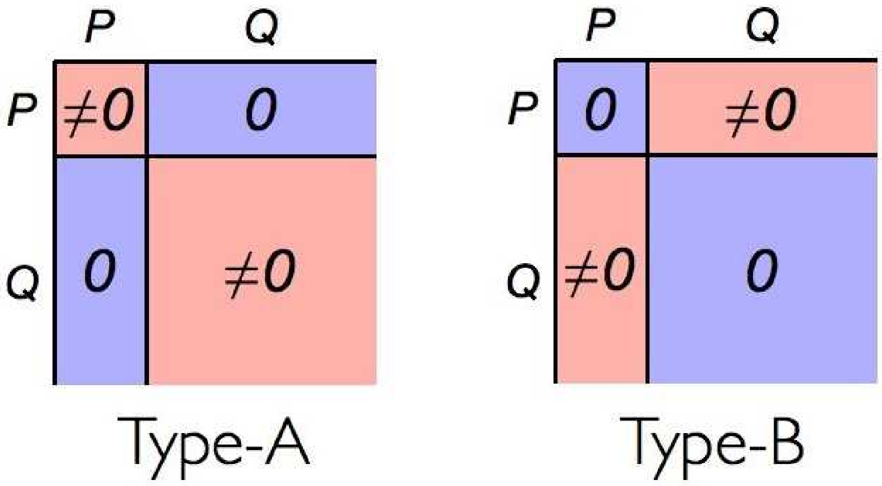

Figure 6.16: Type-A operators preserve the subspace; type B operators change the subspace.

To third order in λ, we will need the following expressions:

$$\begin{aligned}\big[H^0+\lambda V_{\rm A},S\big]_{(1)} &= \lambda\,\big[H^0,S^{(1)}\big] + \lambda^2\Big(\big[H^0,S^{(1)}\big] + \big[V_{\rm A},S^{(1)}\big]\Big)\\ &\qquad\qquad + \lambda^3\Big(\big[H^0,S^{(3)}\big] + \big[V_{\rm A},S^{(2)}\big]\Big) + \mathcal{O}(\lambda^4)\\ \big[H^0+\lambda V_{\rm A},S\big]_{(3)} &= \lambda^3\,\big[\big[\big[H^0,S^{(1)}\big],S^{(1)}\big],S^{(1)}\big] + \mathcal{O}(\lambda^4)\end{aligned} \tag{6.208}$$

and

$$\begin{aligned}\big[\lambda V_{\rm B},S\big]_{(0)} &= \lambda V_{\rm B}\\ \big[\lambda V_{\rm B},S\big]_{(2)} &= \lambda^3\,\big[\big[V_{\rm B},S^{(1)}\big],S^{(1)}\big] + \mathcal{O}(\lambda^4)\end{aligned} \tag{6.209}$$

To order λ^3, then, we make $\widetilde{H}_{\rm B}$ vanish by demanding

$$\begin{aligned}0 &= \big[H^0,S^{(1)}\big] + V_{\rm B}\\ 0 &= \big[H^0,S^{(2)}\big] + \big[V_{\rm A},S^{(1)}\big]\\ 0 &= \big[H^0,S^{(3)}\big] + \big[V_{\rm A},S^{(2)}\big] + \tfrac{1}{6}\Big[\big[[H^0,S^{(1)}],S^{(1)}\big],S^{(1)}\Big] + \tfrac{1}{2}\big[[V_{\rm B},S^{(1)}],S^{(1)}\big] \quad .\end{aligned} \tag{6.210}$$

We solve the first equation for $S^{(1)}$, then plug this into the second to obtain an equation for $S^{(2)}$, the solution of which is used in the third equation to obtain $S^{(3)}$, *etc.* Setting $\lambda = 1$, the Hamiltonian is then

$$\begin{aligned}\widetilde{H} = \widetilde{H}_{\rm A} &= H^0 + V_{\rm A} + \big[V_{\rm B},S^{(1)}\big] + \tfrac{1}{2}\big[[H^0,S^{(1)}],S^{(1)}\big] + \ldots\\ &= H^0 + V_{\rm A} + \tfrac{1}{2}\big[V_{\rm B},S^{(1)}\big] + \ldots \quad .\end{aligned} \tag{6.211}$$

Let a and b index states in P and let n and m index states in Q. The equation for $S^{(1)}$ then yields

$$0 = V_{an} + H^0_{ab}\,S^{(1)}_{bn} - S^{(1)}_{am}\,H^0_{mn} = V_{an} + \big(E^0_a - E^0_n\big)\,S^{(1)}_{an} \quad . \tag{6.212}$$

X	$[X,S]_{(2j)}$	$[X,S]_{(2j+1)}$
type A	type A	type B
type B	type B	type A

Table 6.25: Multiple commutators and their types.

Therefore, we have

$$S^{(1)}_{an}=\frac{V_{an}}{E^0_n-E^0_a}\qquad,\qquad S^{(1)}_{na}=\frac{V_{na}}{E^0_a-E^0_n}\quad. \tag{6.213}$$

Note that V_{an} and V_{na} both come from the $V_{\rm B}$ part of V.

The equation for $S^{(2)}$ may be written in component form as

$$\begin{aligned}0&=H^0_{ab}\,S^{(2)}_{bn}-S^{(2)}_{am}\,H^0_{mn}+V_{ab}\,S^{(1)}_{bn}-S^{(1)}_{am}\,V_{mn}\\&=\big(E^0_a-E^0_n\big)\,S^{(2)}_{an}+\frac{V_{ab}V_{ma}}{E^0_n-E^0_b}-\frac{V_{am}V_{mn}}{E^0_m-E^0_a}\quad.\end{aligned} \tag{6.214}$$

Restoring the summation symbols for added clarity, we then have

$$S^{(2)}_{an}=\frac{1}{E^0_a-E^0_n}\cdot\left(\sum_b\frac{V_{ab}V_{bn}}{E^0_n-E^0_b}-\sum_m\frac{V_{am}V_{mn}}{E^0_m-E^0_a}\right), \tag{6.215}$$

with a corresponding expression for $S^{(2)}_{na}$. At this point, the student should write down the expression for $S^{(2)}_{an}$. The Hamiltonian in the P sector, to this order, is then

$$\begin{aligned}\widetilde{H}_{ab}&=E^0_a\,\delta_{ab}+V_{ab}+\tfrac{1}{2}\big(V_{an}S^{(1)}_{nb}-S^{(1)}_{an}V_{nb}\big)\\&=E^0_a\,\delta_{ab}+V_{ab}+\tfrac{1}{2}\sum_n\left(\frac{1}{E^0_a-E^0_n}+\frac{1}{E^0_b-E^0_n}\right)V_{an}V_{nb}\quad.\end{aligned} \tag{6.216}$$

6.9 Jokes for Chapter Six

MATHEMATICS JOKE : Q: What does the "B" in Benoit B. Mandelbrot stand for? A: Benoit B. Mandelbrot.

GRAMMAR JOKE : A businessman is in Boston for only the second time in his life. On his first visit he had some delicious New England seafood, and he's looking forward to going back to the same restaurant. So he hails a cab, and asks the driver, "I was in Boston a few years ago. Can you take me to Angela's, where I had scrod before?" The driver replies, "You know, lots of people ask me that, but never in the pluperfect subjunctive."

LOGICIAN JOKE : A logician's husband tells his wife, "please go to the grocery store on your way home from work. We need a gallon of milk. And if they have eggs, get a dozen." She returns home with twelve gallons of milk. "What the hell happened?!" asks the husband. "They had eggs," she explained.

MUSICIAN JOKE : A conductor who is preparing for a performance is having trouble finding a good clarinet player. He calls a contractor who tells him, "The only guy I've got is a jazz clarinetist." "I can't stand working with jazz musicians!" says the conductor. "They dress like bums, they're always late, and every one of them has an attitude problem." "Hey, he's all I've got," says the contractor. The conductor is desperate, so he agrees.

The conductor arrives early for the first rehearsal and sees the jazz clarinetist wearing a suit and tie, a pencil resting on his stand, and practicing his part. During the rehearsal, he plays sensitively and writes down all of the conductor's suggestions. At the second rehearsal, the clarinetist plays even better. At the final dress rehearsal, he is absolutely flawless.

During the dress rehearsal break, the conductor tells the orchestra, "I've got an apology to make, and I wanted to do so publicly, because there is a lesson here for us all. I was really dreading having to work with a jazz musician, but I must say that our clarinetist has proven me wrong. He's always neatly dressed, comes early to rehearsal, and he really listened to me and learned his part very well indeed." Turning to the clarinet player the maestro says, "I just wanted to tell you that I truly appreciate your effort and dedication."

The clarinetist replies, "Hey man, it's the least I can do since I can't make the gig."

SPECIAL JOKE FOR CHAPTER SIX : A Mn^{4+} ion walks into a bar. The bartender asks, "would you like a point group?" The ion replies, "better make it a double."[40]

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[40] I made this joke up all by myself. It is term-splitting, if not side-splitting. "They laughed when I said I wanted to be a comedian. Well, nobody is laughing now!"