Symmetries in Quantum ESPRESSO (v.2.2.0)

Andrea Dal Corso
(SISSA - Trieste)

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Chapter 1

Introduction

These notes describe how to exploit symmetry in electronic structure codes. They assume only that the reader knows the basic group theory concepts as applied to quantum mechanics and in particular to solids. I discuss some of the formulas implemented in Quantum ESPRESSO with the hope that these concepts might be useful to those who want to further develop the code. The exposition is divided in two parts. In the first part I will use the space group operations of a solid while in the second part I will consider also the magnetic symmetries and discuss how to treat symmetries that might require time reversal.

1.1 People

These notes have been written by Andrea Dal Corso (SISSA, Trieste).

Disclaimer: These notes contain the concepts that I found useful to understand the symmetry routines of Quantum ESPRESSO, but I am not the author of many of them, so what is written here might be inaccurate or not reflect the original intention of the authors. If you find that something is incorrect or does not reflect what is implemented please e-mail me at dalcorso .at. sissa.it. The concepts presented here have benefited from discussions with several people, among them I would like to thank S. de Gironcoli (and his unpublished notes on the symmetry of the phonon code), A. Smogunov, and A. Urru (and the appendices of his PhD thesis).

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1.2 Preliminary definitions

The equilibrium positions of the atoms in a solid are determined by a Bravais lattice and by the positions of the atoms inside a unit cell.

The Bravais lattice can be defined by three primitive vectors:

$$\mathbf{a}_1, \mathbf{a_2}, \mathbf{a}_3. \tag{1.1}$$

Each point of the lattice is given by three integer values n_1, n_2, n_3 that can be positive, negative, or null. We indicate with $\mathbf{R}_\mu$ the coordinates of the Bravais lattice points:

$$\mathbf{R}_\mu = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \tag{1.2}$$

We indicate with $\boldsymbol{\tau}_s$ the positions of the atoms inside the unit cell ($s = 1, \cdots, N_{at}$). Each atom s within the unit cell has a type that we call $\gamma(s)$. The equilibrium positions of the atoms in the solid are therefore:

$$\mathbf{R}_I = \mathbf{R}_\mu + \boldsymbol{\tau}_s, \tag{1.3}$$

and the index $I = \{\mu, s\}$ is a composite index that indicates both the Bravais lattice and the atom inside the unit cell.

We say that a rototranslation $\{S, \mathbf{a}\}$, where S is a proper (or improper) rotation and $\mathbf{a}$ is a translation, belongs to the solid space group if for any $I = \{\mu, s\}$ there is an $\bar{I} = \{\bar{\mu}, \bar{s}\}$ such that:

$$\{S, \mathbf{a}\}\mathbf{R}_I = S\mathbf{R}_\mu + S\boldsymbol{\tau}_s + \mathbf{a} = \mathbf{R}_{\bar{\mu}} + \boldsymbol{\tau}_{\bar{s}}, \tag{1.4}$$

and $\gamma(s) = \gamma(\bar{s})$.

The operations $\{S_i, \mathbf{a}_i\}$ for which Eq. 1.4 holds form a group. We have:

$$\{S_i, \mathbf{a}_i\}\{S_j, \mathbf{a}_j\} = \{S_iS_j, S_i\mathbf{a}_j + \mathbf{a}_i\}. \tag{1.5}$$

The neutral element of the group is $\{\mathbb{I}, 0\}$ where $\mathbb{I}$ is the identity matrix and 0 is the null translation. The inverse of an element is

$$\{S_i, \mathbf{a}_i\}^{-1} = \{S_i^{-1}, -S_i^{-1}\mathbf{a}_i\}. \tag{1.6}$$

It is useful also to introduce the fractional translations $\mathbf{f}_i$, by considering the vector $\mathbf{R}_{\mu_i}$ closer to $\mathbf{a}_i$ and writing the operations of the space group as

$$\{S_i, \mathbf{a}_i\} = \{S_i, \mathbf{R}_{\mu_i} + \mathbf{f}_i\}. \tag{1.7}$$

The set of rotations $\{S_i\}$ form a group called the solid point group. In general, the set $\{S_i, 0\}$ is not a subgroup of the space group.

1.3 Coordinates

1.3.1 The rotation matrix

There are two ways to express the rotation matrices S of the point group. We can consider the three vectors obtained by application of S to $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$.

They must be Bravais lattice vectors and they can be expressed as

$$\mathbf{a}'_l = \sum_{m=1}^{3} S_{l,m}\mathbf{a}_m, \tag{1.8}$$

where $S_{l,m}$ is a 3×3 integer matrix. Alternatively, we can introduce Cartesian coordinates and write the primitive vectors as $\mathbf{a}_{\alpha,i}$ where α indicates a Cartesian coordinate. We can indicate the Cartesian rotation matrix as $S_{\alpha,\beta}$ and we have:

$$\mathbf{a}'_{\alpha,l} = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{a}_{\beta,l}. \tag{1.9}$$

The matrix $S_{\alpha,\beta}$ is an orthogonal ($S_{\beta,\alpha} = S^{-1}_{\alpha,\beta}$) 3×3 matrix, while $S_{l,m}$ in general is not orthogonal. We can write $S_{\alpha,\beta}$ in terms of $S_{l,m}$ or $S_{l,m}$ in terms of $S_{\alpha,\beta}$ using the following considerations.

Assuming that $\mathbf{a}_m$ are in units of a (the lattice constants), we introduce the primitive reciprocal lattice vector $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ (in units of $\frac{2\pi}{a}$) such that

$$\mathbf{a}_i \cdot \mathbf{b}_j = \sum_{\alpha=1}^{3} \mathbf{a}_{\alpha,i}\mathbf{b}_{\alpha,j} = \delta_{i,j}. \tag{1.10}$$

From this equation one derives also that:

$$\sum_{j=1}^{3} \mathbf{b}_{\alpha,j}\mathbf{a}_{\beta,j} = \delta_{\alpha,\beta}. \tag{1.11}$$

Multiplying Eq. 1.8 by $\mathbf{b}_{\alpha,j}$, summing on α and using Eq. 1.10 we have

$$\sum_{\alpha=1}^{3} \mathbf{a}'_{\alpha,l}\mathbf{b}_{\alpha,j} = S_{l,j}, \tag{1.12}$$

and using Eq. 1.9:

$$S_{l,j} = \sum_{\alpha=1}^{3}\sum_{\beta=1}^{3} \mathbf{b}_{\alpha,j}S_{\alpha,\beta}\mathbf{a}_{\beta,l}. \tag{1.13}$$

The inverse of this equation can be found by multiplying both terms by $\mathbf{a}_{\gamma,j}$ and $\mathbf{b}_{\delta,l}$, summing over j and l and using Eq. 1.11 twice:

$$\sum_{l,j} \mathbf{b}_{\delta,l}S_{l,j}\mathbf{a}_{\gamma,j} = S_{\gamma,\delta}. \tag{1.14}$$

1.3.2 Rotation of a vector

Given the Cartesian coordinates of a vector $\mathbf{v}$, the rotated Cartesian coordinates are:

$$\mathbf{v}'_\alpha = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{v}_\beta. \tag{1.15}$$

When the vector v is expressed in crystal coordinates:

$$\mathbf{v} = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{a}_l. \tag{1.16}$$

the rotated vector can be written as

$$\mathbf{v}' = \sum_{i=1}^{3} \mathbf{v}_l \mathbf{a}'_l. \tag{1.17}$$

and its coordinates can also be written again in the original basis $\mathbf{a}_i$ using Eq. 1.8:

$$\mathbf{v}' = \sum_{l=1}^{3} \sum_{m=1}^{3} \mathbf{v}_l S_{l,m} \mathbf{a}_m, \tag{1.18}$$

with

$$\mathbf{v}'_m = \sum_{l=1}^{3} \mathbf{v}_l S_{l,m}. \tag{1.19}$$

1.3.3 Rotation of a vector in reciprocal space

We can rotate the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$. They must be reciprocal lattice vectors so they can be written as linear combination of $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$:

$$\mathbf{b}'_j = \sum_{m=1}^{3} U_{j,m} \mathbf{b}_m, \tag{1.20}$$

where the matrix $U_{j,m}$ is a 3×3 integer matrix. Since

$$\mathbf{a}'_i \cdot \mathbf{b}'_j = \delta_{i,j}, \tag{1.21}$$

we must have:

$$\sum_{l=1}^{3} \sum_{m=1}^{3} S_{i,l} \mathbf{a}_l \cdot U_{j,m} \mathbf{b}_\mathbf{m} = \sum_{l=1}^{3} S_{i,l} U_{j,l} = \delta_{i,j}. \tag{1.22}$$

From this equation we find that

$$U_{j,l} = S^{-1}_{l,j}, \tag{1.23}$$

where the operator S^{-1} is the inverse of the rotation S, belongs to the point group, and is an integer matrix. The rotated principal reciprocal lattice vectors are:

$$\mathbf{b}'_j = \sum_{m=1}^{3} S^{-1}_{m,j} \mathbf{b}_m. \tag{1.24}$$

With this equation we can rotate a vector v written in the basis of the primitive reciprocal lattice vectors. We have:

$$\mathbf{v} = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{b}_l. \tag{1.25}$$

and the rotated vector is

$$\mathbf{v}' = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{b}'_l, \tag{1.26}$$

or, in the original reciprocal primitive basis:

$$\mathbf{v}' = \sum_{l=1}^{3} \sum_{m=1}^{3} \mathbf{v}_l S^{-1}_{m,l} \mathbf{b}_m. \tag{1.27}$$

So the components of the rotated vector are:

$$\mathbf{v}'_m = \sum_{l=1}^{3} \mathbf{v}_l S^{-1}_{m,l}. \tag{1.28}$$

1.3.4 Basis change

When a vector is given in Cartesian coordinates ($\mathbf{v}_\alpha$) we can write it in the basis of the primitive Bravais lattice vectors. We have:

$$\mathbf{v} = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{a}_l. \tag{1.29}$$

Multiplying both members of this equation by $\mathbf{b}_m$ we get

$$\mathbf{v}_m = \mathbf{v} \cdot \mathbf{b}_m = \sum_{\alpha=1}^{3} \mathbf{v}_\alpha \mathbf{b}_{\alpha,m}. \tag{1.30}$$

When a vector is given in Cartesian coordinates ($\mathbf{v}_\alpha$) we can write it in the basis of the primitive reciprocal lattice vectors:

$$\mathbf{v} = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{b}_l. \tag{1.31}$$

Multiplying both members of this equation by $\mathbf{a}_m$ we get

$$\mathbf{v}_m = \mathbf{v} \cdot \mathbf{a}_m = \sum_{\alpha=1}^{3} \mathbf{v}_\alpha \mathbf{a}_{\alpha,m}. \tag{1.32}$$

When a vector is given in the basis of the primitive Bravais lattice vectors its Cartesian coordinates are

$$\mathbf{v}_\alpha = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{a}_{\alpha,l}. \tag{1.33}$$

When a vector is given in the basis of the primitive reciprocal lattice vectors its Cartesian coordinates are

$$\mathbf{v}_\alpha = \sum_{l=1}^{3} \mathbf{v}_l \mathbf{b}_{\alpha,l}. \tag{1.34}$$

Chapter 2

Symmetry in self-consistent codes

2.1 The Kohn and Sham wavefunctions

We can consider the Bloch functions, solutions of the Kohn and Sham equations:

$$H_{KS}\psi_{\mathbf{k},n}(\mathbf{r}) = \varepsilon_{\mathbf{k},n}\psi_{\mathbf{k},n}(\mathbf{r}), \tag{2.1}$$

where k is a wave vector in the first Brillouin zone an n is a band index. For each element of the space group $\{S_i, \mathbf{a}_i\}$ we can associate an operator $O_{\{S_i,\mathbf{a}_i\}}$ that rotates the Bloch functions. We require that after the rotation the new function $O_{\{S_i,\mathbf{a}_i\}}\psi_{\mathbf{k}n}(\mathbf{r})$ has in r the same value that the original function had in the point r′ that becomes r after the rotation. We have

$$\mathbf{r}' = \{S_i, \mathbf{a}_i\}^{-1}\mathbf{r} \tag{2.2}$$

therefore

$$O_{\{S_i,\mathbf{a}_i\}}\psi_{\mathbf{k},n}(\mathbf{r}) = \psi_{\mathbf{k},n}(\{S_i, \mathbf{a}_i\}^{-1}\mathbf{r}). \tag{2.3}$$

Writing the Bloch functions in the form

$$\psi_{\mathbf{k},n}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k},n}(\mathbf{r}), \tag{2.4}$$

where $u_{\mathbf{k},n}(\mathbf{r})$ is a lattice periodic function, we have:

$$O_{\{S_i,\mathbf{a}_i\}}\psi_{\mathbf{k},n}(\mathbf{r}) = e^{iS_i\mathbf{k}\cdot\mathbf{r}}e^{-iS_i\mathbf{k}\cdot\mathbf{a}_i}u_{\mathbf{k},n}(\{S_i, \mathbf{a}_i\}^{-1}\mathbf{r}). \tag{2.5}$$

Therefore, $O_{\{S_i,\mathbf{a}_i\}}\psi_{\mathbf{k},n}(\mathbf{r})$ is a Bloch function with wave-vector $S_i\mathbf{k}$. If $\{S_i, \mathbf{a}_i\}$ belongs to the solid space group, $O_{\{S_i,\mathbf{a}_i\}}$ commutes with H_{KS} and $O_{\{S_i,\mathbf{a}_i\}}\psi_{\mathbf{k},n}(\mathbf{r})$ is an eigenstate with eigenvalue $\varepsilon_{\mathbf{k},n}$. We can call it $\psi_{S_i\mathbf{k},n}(\mathbf{r})$.

2.2 The charge density in real space

The charge density is calculated as a sum over the Brillouin zone and the occupied bands:

$$n(\mathbf{r}) = 2\sum_{\mathbf{k},v}|\psi_{\mathbf{k},v}(\mathbf{r})|^2, \tag{2.6}$$

where the factor two accounts for spin degeneracy. Usually we use a uniform grid $N_{k_1} \times N_{k_2} \times N_{k_3}$ of k of points to perform this sum, and we use a grid such that if we apply a rotation S_i of the point group to a wave-vector k we obtain the wave-vector S_ik which belongs to the grid. In these hypotheses, the set of wave vectors S_ik obtained by applying S_i to all points of the grid coincides with the original grid itself. Therefore we can write

$$n(\mathbf{r}) = \frac{2}{N_S} \sum_{i=1}^{N_S} \sum_{\mathbf{k},v} |\psi_{S_i\mathbf{k},v}(\mathbf{r})|^2, \tag{2.7}$$

where N_S is the number of symmetries of the point group. Now each k in the mesh can be obtained from a k in the irreducible Brillouin zone (IBZ) by applying an appropriate rotation S_l. We can write:

$$n(\mathbf{r}) = \frac{2}{N_S} \sum_{i=1}^{N_S} \sum_{\mathbf{k}\in IBZ,v} \sum_{l} |\psi_{S_iS_l\mathbf{k},v}(\mathbf{r})|^2. \tag{2.8}$$

The sum over k is limited to the IBZ and the sum over l is over the $N_\mathbf{k}$ symmetries needed to obtain all the points of the star of k that belong to the mesh from the k in the IBZ. But now we can exchange the sum over l and the sum over i and notice that the sum over i is over all the elements of the point group and for the rearrangement lemma the elements $\{S_iS_l\}$ are still all the elements of the point group so the sum over i is independent from l. It is convenient to introduce a weight $w_\mathbf{k}$ (see next section for a more precise definition) so that we can write

$$n(\mathbf{r}) = \frac{2}{N_S} \sum_{i=1}^{N_S} \sum_{\mathbf{k}\in IBZ,v} w_\mathbf{k}\ |\psi_{S_i\mathbf{k},v}(\mathbf{r})|^2. \tag{2.9}$$

Now we can use Eq. 2.5 and write

$$n(\mathbf{r}) = \frac{2}{N_S} \sum_{i=1}^{N_S} \sum_{\mathbf{k}\in IBZ,v} w_\mathbf{k}\ |\psi_{\mathbf{k},v}(\{S_i,\mathbf{f}_i\}^{-1}\mathbf{r})|^2, \tag{2.10}$$

where we choose the spatial group operation $\{S_i,\mathbf{f}_i\}$ since Eq. 2.10 does not depend on $\mathbf{R}_{\mu_i}$.

The charge density is computed in two steps. First one computes the unsymmetrized charge density:

$$\tilde{n}(\mathbf{r}) = 2 \sum_{\mathbf{k}\in IBZ,v} w_\mathbf{k}\ |\psi_{\mathbf{k},v}(\mathbf{r})|^2, \tag{2.11}$$

and finally the charge density is symmetrized:

$$n(\mathbf{r}) = \frac{1}{N_S} \sum_{i=1}^{N_S} \tilde{n}(\{S_i,\mathbf{f}_i\}^{-1}\mathbf{r}). \tag{2.12}$$

Since we are adding on all operations of the group, we obtain the same result applying $\{S_i,\mathbf{f}_i\}$ in Eq. 2.12:

$$n(\mathbf{r}) = \frac{1}{N_S} \sum_{i=1}^{N_S} \tilde{n}(\{S_i,\mathbf{f}_i\}\mathbf{r}). \tag{2.13}$$

2.3 The special point technique

Suppose we have a function of the reciprocal lattice vector $g(\mathbf{k})$, periodic with the periodicity of the reciprocal lattice vectors G. We can expand this function in Fourier series:

$$g(\mathbf{k}) = g_0 + \sum_{\mu} g_\mu e^{i\mathbf{k}\cdot\mathbf{R}_\mu}, \tag{2.14}$$

$\mathbf{R}_\mu$ are the direct lattice vectors (where $\mathbf{R}_\mu = 0$ has been separated from the sum). Suppose G is the point group of the Bravais lattice and h the number of symmetry elements of $G = \{S_1, ..., S_h\}$. We can consider the symmetric function

$$f(\mathbf{k}) = \frac{1}{h}\sum_{i=1}^{h} g(S_i\mathbf{k}) \tag{2.15}$$

We have

$$f(\mathbf{k}) = f_0 + \sum_{\mu} g_\mu A_\mu(\mathbf{k}) \tag{2.16}$$

where $f_0 = g_0$ and

$$A_\mu(\mathbf{k}) = \frac{1}{h}\sum_{i=1}^{h} e^{iS_i\mathbf{k}\cdot\mathbf{R}_\mu} = \frac{1}{h}\sum_{i=1}^{h} e^{i\mathbf{k}\cdot S_i^{-1}\mathbf{R}_\mu}. \tag{2.17}$$

The integral over the Brillouin zone of $A_\mu(\mathbf{k}) = 0$ for all μ except $\mu = 0$ hence the average over the Brillouin zone of $f(\mathbf{k})$ and of $g(\mathbf{k})$ coincide:

$$\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k g(\mathbf{k}) = \frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k f(\mathbf{k}) = f_0. \tag{2.18}$$

The integral is discretized with a uniform mesh of $N_\mathbf{k} = N_1 \times N_2 \times N_3$ points (see the routine `kpoint_grid`) and therefore one calculates the sum

$$\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k f(\mathbf{k}) = \frac{1}{N_\mathbf{k} h}\sum_{j=1}^{N_\mathbf{k}}\sum_{i=1}^{h} g(S_i\mathbf{k}_j). \tag{2.19}$$

The mesh is usually chosen in such a way to set to zero the largest number of functions $A_\mu(\mathbf{k})$. In practice however one chooses a uniform mesh. All the points $\mathbf{k}_j$ that belong to the same star of k give the same contribution to the sum (Eq. 2.19). So we can take only one point in the irreducible Brillouin zone (reduced with the Bravais lattice point group) (IBZ_L) and put a weight equal to the number of $\mathbf{k}$ point of the star of $\mathbf{k}_j$ that belong to the original mesh. We obtain

$$\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k f(\mathbf{k}) = \frac{1}{N_\mathbf{k} h}\sum_{j\in IBZ_L} w_j \sum_{i=1}^{h} g(S_i\mathbf{k}_j) = \frac{1}{h}\sum_{j\in IBZ_L} \tilde{w}_j \sum_{i=1}^{h} g(S_i\mathbf{k}_j), \tag{2.20}$$

where in the last term $\tilde{w}_j = w_j/N_\mathbf{k}$ and the sum over all weights is equal to one.

We note that the function $g(\mathbf{k})$ has usually the symmetry of the solid, or as in the case of the charge density one can relate the values of $g(S_i\mathbf{k}_j)$ at one point $\mathbf{r}$ with those of a different point $\mathbf{r}'$, but only for the operations of the point group of the solid which is usually a subgroup of G. We call it H, with elements S_p with $p = 1, ..., k$. It is convenient then to divide the group G into $N_c = h/k$ left cosets of H (see the routine `coset` for a definition):

$$G = H + S_iH + S_lH + ... + S_{N_c}H. \tag{2.21}$$

When we apply the operations of H to a $\mathbf{k}_j$ point we obtain the star of $\mathbf{k}_j$ (according to the group H) which is usually smaller than the star of $\mathbf{k}_j$ for the group G. So he have:

$$\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k f(\mathbf{k}) = \frac{1}{h}\sum_{j\in IBZ_L}\tilde{w}_j\sum_{l=1}^{N_c}\sum_{p=1}^{k} g(S_lS_p\mathbf{k}_j). \tag{2.22}$$

Now when we apply all the operations of H to $S_l\mathbf{k}_j$ we obtain the star of $S_l\mathbf{k}_j$ for the group H. All the points of this star give the same contribution to this sum. Therefore, we can take only one point $\mathbf{k}_m$ in the irreducible brillouin zone (reduced with the solid point group) (IBZ_S) and put a weight equal to $\tilde{w}_j$ multiplied by the number of times we find the same star varying S_l among the N_c cosets $w(m)$.

$$\frac{\Omega}{(2\pi)^3}\int_{BZ} d^3k f(\mathbf{k}) = \frac{1}{h}\sum_{m\in IBZ_S}\tilde{w}_m\sum_{p=1}^{k} g(S_p\mathbf{k}_m) = \frac{1}{k}\sum_{p=1}^{k}\sum_{m\in IBZ_S}\bar{w}_m g(S_p\mathbf{k}_m), \tag{2.23}$$

where $\tilde{w}_m = \tilde{w}_j w(m)$ and $\bar{w}_m = \frac{\tilde{w}_m}{N_c}$. This equation coincides with Eq. 2.9 taking

$$g(\mathbf{k}) = 2|\psi_{\mathbf{k},v}(\mathbf{r})|^2, \tag{2.24}$$

and defines how one has to calculate the weights that appear in that equation.

2.4 The charge density in reciprocal space

Eq. 2.13 can be used to find a symmetrization formula in reciprocal space. Taking the Fourier transform at the reciprocal lattice vector G, we have:

$$\begin{aligned} n(\mathbf{G}) &= \frac{1}{N_S}\frac{1}{\Omega}\sum_{i=1}^{N_S}\int_\Omega \tilde{n}(\{S_i,\mathbf{f}_i\}\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d^3r \\ &= \frac{1}{N_S}\frac{1}{\Omega}\sum_{i=1}^{N_S}\int_\Omega \tilde{n}(\mathbf{r})e^{-i\mathbf{G}\cdot\{S_i,\mathbf{f}_i\}^{-1}\mathbf{r}}d^3r \\ &= \frac{1}{N_S}\frac{1}{\Omega}\sum_{i=1}^{N_S}\int_\Omega \tilde{n}(\mathbf{r})e^{-i\mathbf{G}\cdot S_i^{-1}\mathbf{r}}e^{i\mathbf{G}\cdot S_i^{-1}\mathbf{f}_i}d^3r \\ &= \frac{1}{N_S}\frac{1}{\Omega}\sum_{i=1}^{N_S}e^{iS_i\mathbf{G}\cdot\mathbf{f}_i}\int_\Omega \tilde{n}(\mathbf{r})e^{-iS_i\mathbf{G}\cdot\mathbf{r}}d^3r \\ &= \frac{1}{N_S}\sum_{i=1}^{N_S}e^{iS_i\mathbf{G}\cdot\mathbf{f}_i}\tilde{n}(S_i\mathbf{G}). \end{aligned} \tag{2.25}$$

This formula could be applied for any G vector but it useful to observe that if we know $n(\mathbf{G})$ we can find $n(S_i\mathbf{G})$ with a simple formula. Since after an operation of the space group $\{S_i,\mathbf{f}_i\}$ the solid does not change we must have:

$$n(\mathbf{r}) = n(\{S_i,\mathbf{f}_i\}\mathbf{r}). \tag{2.26}$$

Doing a Fourier transform as shown above, from this formula we get

$$n(\mathbf{G}) = e^{iS_i\mathbf{G}\cdot\mathbf{f}_i}n(S_i\mathbf{G}), \tag{2.27}$$

or

$$n(S_i\mathbf{G}) = e^{-iS_i\mathbf{G}\cdot\mathbf{f}_i}n(\mathbf{G}). \tag{2.28}$$

2.5 The forces

Let us now consider a set of displacements of each atom of the solid. We indicate with $\mathbf{u}_I$ the displacement of the atom that in equilibrium is in $\mathbf{R}_I$. Suppose that we compute the total energy with the atomic coordinates $\{\mathbf{R}_I + \mathbf{u}_I\}$. If we do an opertion of the solid space group $\{S_i,\mathbf{a}_i\}$ the atomic positions becomes

$$\{S_i,\mathbf{a}_i\}(\mathbf{R}_I+\mathbf{u}_I) = \mathbf{R}_{\bar{I}} + S_i\mathbf{u}_I. \tag{2.29}$$

So if in the rotated solids we choose the displacements

$$\mathbf{u}'_{\bar{I}} = S_i\mathbf{u}_I, \tag{2.30}$$

the energy cannot change and we can write:

$$E_{tot}\left(\{\mathbf{R}_I+\mathbf{u}_I\}\right) = E_{tot}\left(\{\{S_i,\mathbf{a}_i\}(\mathbf{R}_I+\mathbf{u}_I)\}\right) = E_{tot}\left(\{\mathbf{R}_{\bar{I}}+\mathbf{u}'_{\bar{I}}\}\right). \tag{2.31}$$

Computing the derivatives with respect to $\mathbf{u}_{I,\alpha}$ we have:

$$\frac{dE_{tot}}{d\mathbf{u}_{\mu,s,\alpha}} = \sum_{\beta=1}^{3} \frac{dE_{tot}}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}} \frac{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}{d\mathbf{u}_{\mu,s,\alpha}} = \sum_{\beta=1}^{3} \frac{dE_{tot}}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}} S_{i,\beta,\alpha} = \sum_{\beta=1}^{3} S^{-1}_{i,\alpha,\beta} \frac{dE_{tot}}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}, \tag{2.32}$$

where we used the fact that $S_{i,\alpha,\beta}$ is an orthogonal matrix.

This relation can be used by adding on all the operations of the point group S_i and dividing by N_S. In the left hand side that does not depend on S_i we obtain the symmetrised forces:

$$\mathbf{F}_{s,\alpha} = \frac{1}{N_S} \sum_{i=1}^{N_S} \sum_{\beta=1}^{3} S^{-1}_{i,\alpha,\beta} \mathbf{F}_{\bar{s},\beta}. \tag{2.33}$$

In the right-hand side, we can use the unsymmetrized forces computed by doing a sum over the IBZ when adding on k.

Reasoning in the same way we can write a similar relationship for the second derivative of the energy with respect to two displacements:

$$\frac{d^2E_{tot}}{d\mathbf{u}_{\mu,s,\alpha} d\mathbf{u}_{\nu,s',\beta}} = \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} \frac{d^2E_{tot}}{d\mathbf{u}_{\bar{\mu},\bar{s},\gamma} d\mathbf{u}_{\bar{\nu},\bar{s}',\delta}}. \tag{2.34}$$

2.6 The stress

The stress is defined as the derivative of the total energy with respect to strain:

$$\sigma_{\alpha,\beta} = \frac{1}{V} \frac{\partial E_{tot}}{\partial \varepsilon_{\alpha,\beta}}. \tag{2.35}$$

If we rotate the solid with an operation $\{S, \mathbf{a}\}$ of the solid space group, the total energy does not change if we put a rotated strain. Since the strain is a second rank tensor we must put a strain

$$\varepsilon'_{\alpha,\beta} = \sum_{\gamma,\delta} S_{\alpha,\gamma} S_{\beta,\delta} \varepsilon_{\gamma,\delta}. \tag{2.36}$$

With this strain we can write

$$E_{tot}\left(\{\varepsilon_{\alpha,\beta}\}\right) = E_{tot}\left(\{\varepsilon'_{\alpha,\beta}\}\right), \tag{2.37}$$

and doing the derivatives we have:

$$\frac{\partial E_{tot}\left(\{\varepsilon_{\alpha,\beta}\}\right)}{\partial \varepsilon_{\alpha,\beta}} = \sum_{\gamma,\delta=1}^{3} \frac{\partial E_{tot}\left(\{\varepsilon'_{\alpha,\beta}\}\right)}{\partial \varepsilon'_{\gamma,\delta}} \frac{\partial \varepsilon'_{\gamma,\delta}}{\partial \varepsilon_{\alpha,\beta}} = \sum_{\gamma,\delta=1}^{3} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} \frac{\partial E_{tot}\left(\{\varepsilon'_{\alpha,\beta}\}\right)}{\partial \varepsilon'_{\gamma,\delta}}. \tag{2.38}$$

Equivalently we can write:

$$\sigma_{\alpha,\beta} = \sum_{\gamma,\delta=1}^{3} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} \sigma_{\gamma,\delta}. \tag{2.39}$$

The working symmetrization formula is obtained adding on the N_S symmetry operations of the point group and dividing by N_S. We have:

$$\sigma_{\alpha,\beta} = \frac{1}{N_S} \sum_{i=1}^{3} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} \sigma_{\gamma,\delta}. \tag{2.40}$$

Chapter 3

Symmetry in linear response codes

3.1 Dynamical matrix

The dynamical matrix is defined in term of the interatomic force constants by the relationship:

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N\sqrt{M_s M'_s}} \sum_{\mu} \sum_{\nu} e^{-i\mathbf{q}\cdot\mathbf{R}_\mu} \frac{d^2 E_{tot}}{d\mathbf{u}_{\mu,s,\alpha} d\mathbf{u}_{\nu,s',\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_\nu}. \tag{3.1}$$

We can insert a sum over $\bar{\mu}$ and a sum over $\bar{\nu}$ and divide by N^2. We have

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N^3\sqrt{M_s M'_s}} \sum_{\mu,\bar{\mu}} \sum_{\nu,\bar{\nu}} e^{-i\mathbf{q}\cdot(\mathbf{R}_\mu - S^{-1}\mathbf{R}_{\bar{\mu}})} e^{-iS\mathbf{q}\cdot\mathbf{R}_{\bar{\mu}}} \frac{d^2 E_{tot}}{d\mathbf{u}_{\mu,s,\alpha} d\mathbf{u}_{\nu,s',\beta}} e^{iS\mathbf{q}\cdot\mathbf{R}_{\bar{\nu}}} e^{i\mathbf{q}\cdot(\mathbf{R}_\nu - S^{-1}\mathbf{R}_{\bar{\nu}})} \tag{3.2}$$

and now we can use Eq.2.34 to write

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N^3\sqrt{M_s M'_s}} \sum_{\mu,\bar{\mu},\nu,\bar{\nu}} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} e^{-i\mathbf{q}\cdot(\mathbf{R}_\mu - S^{-1}\mathbf{R}_{\bar{\mu}})} \times e^{-iS\mathbf{q}\cdot\mathbf{R}_{\bar{\mu}}} \frac{d^2 E_{tot}}{d\mathbf{u}_{\bar{\mu},\bar{s},\gamma} d\mathbf{u}_{\bar{\nu},\bar{s}',\delta}} e^{iS\mathbf{q}\cdot\mathbf{R}_{\bar{\nu}}} e^{i\mathbf{q}\cdot(\mathbf{R}_\nu - S^{-1}\mathbf{R}_{\bar{\nu}})} \tag{3.3}$$

or

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N^2} \sum_{\mu,\nu} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} e^{-i\mathbf{q}\cdot(\mathbf{R}_\mu - S^{-1}\mathbf{R}_{\bar{\mu}})} D_{\bar{s},\gamma,\bar{s}',\delta}(S\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{R}_\nu - S^{-1}\mathbf{R}_{\bar{\nu}})}. \tag{3.4}$$

If $\{S, \mathbf{a}\}$ is an operation of the solid space group we have:

$$\{S, \mathbf{a}\}(\mathbf{R}_\mu + \boldsymbol{\tau}_s) = S\mathbf{R}_\mu + S\boldsymbol{\tau}_s + \mathbf{a} = \mathbf{R}_{\bar{\mu}} + \boldsymbol{\tau}_{\bar{s}}, \tag{3.5}$$

or

$$S\mathbf{R}_\mu - \mathbf{R}_{\bar{\mu}} = -S\boldsymbol{\tau}_s + \boldsymbol{\tau}_{\bar{s}} - \mathbf{a}, \tag{3.6}$$

and

$$S\mathbf{R}_\nu - \mathbf{R}_{\bar{\nu}} = -S\boldsymbol{\tau}_{s'} + \boldsymbol{\tau}_{\bar{s}'} - \mathbf{a}. \tag{3.7}$$

Calling

$$\mathbf{R}^S_{\boldsymbol{\tau}_s} = S\boldsymbol{\tau}_s - \boldsymbol{\tau}_{\bar{s}}, \tag{3.8}$$

we obtain the equation:

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} e^{iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} D_{\bar{s},\gamma,\bar{s}',\delta}(S\mathbf{q}) e^{-iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}}. \tag{3.9}$$

This expression tell us the equations satisfied by the dynamical matrix elements. Its inverse can be obtained easily:

$$D_{\bar{s},\alpha,\bar{s}',\beta}(S\mathbf{q}) = \sum_{\gamma,\delta=1}^{3} S_{\alpha,\gamma} S_{\beta,\delta} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} D_{s,\gamma,s',\delta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}}, \tag{3.10}$$

and gives as an equation to find the dynamical matrix at $S\mathbf{q}$ if we know the dynamical matrix at $\mathbf{q}$. Eq. 3.9 can be used in the form:

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N_S} \sum_{i=1}^{N_S} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} e^{iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} \tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(S\mathbf{q}) e^{-iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}}, \tag{3.11}$$

to symmetrize a dynamical matrix obtained by doing sums over the $\mathbf{k}$ points in the IBZ. Usually in this case we reduce the $\mathbf{k}$ points using only the symmetries of the cogroup of $\mathbf{q}$ that is only the rotations for which

$$S\mathbf{q} = \mathbf{q} + \mathbf{G}_S \tag{3.12}$$

where $\mathbf{G}_S$ is a reciprocal lattice vectors. Eq. 3.11 simplifies as:

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N_{S_\mathbf{q}}} \sum_{i=1}^{N_{S_\mathbf{q}}} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} \tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q}) e^{i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s} - \mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)}, \tag{3.13}$$

where we used the fact that the dynamical matrix as a function of $\mathbf{q}$ is periodic with the periodicity of the reciprocal lattice, and $\mathbf{R}^S_{\boldsymbol{\tau}_s} + \mathbf{a}$ is a Bravais lattice vector.

Also Eq. 3.10 can be specialized to the symmetries of the cogroup of $\mathbf{q}$

$$D_{\bar{s},\alpha,\bar{s}',\beta}(\mathbf{q}) = \sum_{\gamma,\delta=1}^{3} S_{i,\alpha,\gamma} S_{i,\beta,\delta} D_{s,\gamma,s',\delta}(\mathbf{q}) e^{-i\mathbf{q}\cdot(\mathbf{R}^S_{\boldsymbol{\tau}_s} - \mathbf{R}^S_{\boldsymbol{\tau}_{s'}})}, \tag{3.14}$$

and used to calculate all the matrix elements $D_{\bar{s},\alpha,\bar{s}',\beta}(\mathbf{q})$ once we have calculated $D_{s,\alpha,s',\beta}(\mathbf{q})$ with Eq. 3.13.

3.1.1 Eigenvectors of the dynamical matrix

We have seen (in the section on forces) how the displacements in the rotated system are related to those in the original solid. We can find also the relationship between the eigenvectors of the dynamical matrix in the rotated system. A phonon displacement has the form:

$$\mathbf{u}_{\mu,s,\alpha} = \mathbf{u}_{s,\alpha}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_\mu}. \tag{3.15}$$

In the rotated system we must have a similar equation

$$\mathbf{u}'_{\bar{\mu},\bar{s},\alpha} = \mathbf{u}'_{\bar{s},\alpha}(\mathbf{q}')e^{i\mathbf{q}'\cdot\mathbf{R}_{\bar{\mu}}} = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{u}_{\mu,s,\beta} = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{u}_{s,\beta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_{\mu}}. \tag{3.16}$$

We can rewrite this equation in the form

$$\mathbf{u}'_{\bar{\mu},\bar{s},\alpha} = \mathbf{u}'_{\bar{s},\alpha}(\mathbf{q}')e^{i\mathbf{q}'\cdot\mathbf{R}_{\bar{\mu}}} = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{u}_{s,\beta}(\mathbf{q})e^{iS\mathbf{q}\cdot\mathbf{R}_{\bar{\mu}}}e^{i\mathbf{q}\cdot(\mathbf{R}_{\mu}-S^{-1}\mathbf{R}_{\bar{\mu}})}, \tag{3.17}$$

and using the quantity $\mathbf{R}^{S}_{\boldsymbol{\tau}_s}$ (see Eq. 3.8), we can write Eq. 3.17 as

$$\mathbf{u}'_{\bar{s},\alpha}(\mathbf{q}')e^{i\mathbf{q}'\cdot\mathbf{R}_{\bar{\mu}}} = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{u}_{s,\beta}(\mathbf{q})e^{iS\mathbf{q}\cdot\mathbf{R}_{\bar{\mu}}}e^{-iS\mathbf{q}\cdot\left(\mathbf{R}^{S}_{\boldsymbol{\tau}_s}+\mathbf{a}\right)}. \tag{3.18}$$

This shows that $\mathbf{q}' = S\mathbf{q}$ and

$$\mathbf{u}'_{\bar{s},\alpha}(S\mathbf{q}) = \sum_{\beta=1}^{3} S_{\alpha,\beta}\mathbf{u}_{s,\beta}(\mathbf{q})e^{-iS\mathbf{q}\cdot\mathbf{R}^{S}_{\boldsymbol{\tau}_s}}e^{-iS\mathbf{q}\cdot\mathbf{a}}. \tag{3.19}$$

3.2 The charge density induced by a phonon

To symmetrize the charge density induced by a phonon perturbation we consider a space-group operation $\{S,\mathbf{a}\}$ and the charge density in the rotated system. If we look in the point $\{S,\mathbf{a}\}\mathbf{r}$ in the rotated system we should have the same charge as in the point $\mathbf{r}$ in the original system provided that we use Eq. 2.30 for the displacements. Therefore

$$n\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right) = n\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right). \tag{3.20}$$

Deriving with respect to $\mathbf{u}_{\mu,s,\alpha}$ we get

$$\begin{aligned}\frac{dn\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\mu,s,\alpha}} &= \sum_{\beta=1}^{3}\frac{dn\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}\frac{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}{d\mathbf{u}_{\mu,s,\alpha}} \\ &= \sum_{\beta=1}^{3} S^{-1}_{\alpha,\beta}\frac{dn\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}.\end{aligned} \tag{3.21}$$

The charge density induced by a phonon of wave vector $\mathbf{q}$ is given by

$$\frac{dn\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} = \sum_{\mu}\frac{dn\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\mu,s,\alpha}}e^{i\mathbf{q}\cdot\mathbf{R}_{\mu}}, \tag{3.22}$$

and using Eq. 3.21 we obtain:

$$\begin{aligned}\frac{dn\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} &= \frac{1}{N}\sum_{\mu,\bar{\mu}}\sum_{\beta=1}^{3} S^{-1}_{\alpha,\beta}\frac{dn\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\mu},\bar{s},\beta}}e^{iS\mathbf{q}\cdot\mathbf{R}_{\bar{\mu}}}e^{i\mathbf{q}\cdot(\mathbf{R}_{\mu}-S^{-1}\mathbf{R}_{\bar{\mu}})} \\ &= \sum_{\beta=1}^{3} S^{-1}_{\alpha,\beta}\frac{dn\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(S\mathbf{q})}e^{-iS\mathbf{q}\cdot\mathbf{R}^{S}_{\boldsymbol{\tau}_s}}e^{-iS\mathbf{q}\cdot\mathbf{a}},\end{aligned} \tag{3.23}$$

where $\mathbf{R}^S_{\boldsymbol{\tau}_s}$ is defined in Eq. 3.8.

The charge density induced by a phonon can be written as:

$$\frac{dn\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{i\mathbf{q}\cdot\mathbf{r}}\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}, \tag{3.24}$$

where $\frac{d\tilde{n}(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\})}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}$ is a lattice periodic function. We need to symmetrize only the lattice periodic part of the induced charge density, so we have

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}e^{iS\mathbf{q}\cdot\{S,\mathbf{a}\}\mathbf{r}}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(S\mathbf{q})}e^{-iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}e^{-iS\mathbf{q}\cdot\mathbf{a}}, \tag{3.25}$$

This expression can be simplified if we use it for rotations that belong to the small cogroup of $\mathbf{q}$, such that $S\mathbf{q}=\mathbf{q}+\mathbf{G}_S$. Since $\mathbf{R}^S_{\boldsymbol{\tau}_s}+\mathbf{a}$ is a lattice vector we have

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}e^{iS\mathbf{q}\cdot\mathbf{a}}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(S\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}e^{-i\mathbf{q}\cdot\mathbf{a}}. \tag{3.26}$$

Now using the fact that

$$\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q}+\mathbf{G}_S)}=e^{-i\mathbf{G}_S\cdot(S\mathbf{r}+\mathbf{a})}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})}. \tag{3.27}$$

we have

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{-iS^{-1}\mathbf{G}_S\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}. \tag{3.28}$$

This equation can be written also as

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}. \tag{3.29}$$

using the fact that $S^{-1}\mathbf{G}_S=-\mathbf{G}_{S^{-1}}$ as can be deduced comparing the two expressions:

$$\begin{aligned} S\mathbf{q} &= \mathbf{q}+\mathbf{G}_S \\ S^{-1}\mathbf{q} &= \mathbf{q}+\mathbf{G}_{S^{-1}} \end{aligned} \tag{3.30}$$

after applying S^{-1} to the first.

This equation is further transformed before implementation (see the Appendix on irrep).

3.3 The charge density induced by an electric field

Reasoning as above we can say that if $\{S, \mathbf{a}\}$ is a space group operation the charge density at the point $\mathbf{r}$ when there is an electric field $\mathbf{E}$ is equal to the charge density at the rotated point $\{S, \mathbf{a}\}\mathbf{r}$ when the electric field is $\mathbf{E}' = S\mathbf{E}$. Therefore

$$n\left(\mathbf{r}, \mathbf{E}\right) = n\left(\{S, \mathbf{a}\}\mathbf{r}, \mathbf{E}'\right), \tag{3.31}$$

and deriving with respect to $\mathbf{E}_\alpha$ we get

$$\frac{dn\left(\mathbf{r}, \mathbf{E}\right)}{d\mathbf{E}_\alpha} = \sum_{\beta=1}^{3} S^{-1}_{\alpha,\beta} \frac{dn\left(\{S, \mathbf{a}\}\mathbf{r}, \mathbf{E}'\right)}{d\mathbf{E}'_\beta}. \tag{3.32}$$

3.4 The dielectric constant

The dielectric constant can be written as

$$\epsilon_{\alpha,\beta} = \delta_{\alpha,\beta} - \frac{4\pi}{V} \frac{\partial^2 E_{tot}(\mathbf{E})}{\partial \mathbf{E}_\alpha \partial \mathbf{E}_\beta}. \tag{3.33}$$

For an operation $\{S, \mathbf{a}\}$ of the solid space group and a rotated electric field to $\mathbf{E}' = S\mathbf{E}$, the total energy in the rotated system does not change. We have therefore:

$$\frac{\partial^2 E_{tot}(\mathbf{E})}{\partial \mathbf{E}_\alpha \partial \mathbf{E}_\beta} = \sum_{\gamma,\delta=1}^{3} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} \frac{\partial^2 E_{tot}(\mathbf{E}')}{\partial \mathbf{E}'_\gamma \partial \mathbf{E}'_\delta}, \tag{3.34}$$

or equivalently we can write

$$\epsilon_{\alpha,\beta} = \sum_{\gamma,\delta=1}^{3} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} \epsilon_{\gamma,\delta}. \tag{3.35}$$

The working symmetrization formula is obtained adding on the N_S symmetry operations of the point group and dividing by N_S. We have:

$$\epsilon_{\alpha,\beta} = \frac{1}{N_S} \sum_{i=1}^{3} \sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma} S^{-1}_{i,\beta,\delta} \epsilon_{\gamma,\delta}. \tag{3.36}$$

3.5 The Born effective charges

Born effective charges are second derivative of the total energy with respect to phonon displacements and electric field component:

$$qZ^*_{s,\alpha,\beta} = \frac{1}{N} \frac{\partial E_{tot}}{\partial \mathbf{u}_{s,\alpha} \partial \mathbf{E}_\beta}. \tag{3.37}$$

So we use the fact that for an operation $\{S, \mathbf{a}\}$ of the point group of the solid in which the atoms goes in $\{S, \mathbf{a}\}(\mathbf{R}_I + \mathbf{u}_I)$ and the electric field becomes $\mathbf{E}' = S\mathbf{E}$ the total energy should not change.

$$E_{tot}(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E}) = E_{tot}(\{\{S, \mathbf{a}\}(\mathbf{R}_I + \mathbf{u}_I)\}, \mathbf{E}'), \tag{3.38}$$

and performing the derivatives we have:

$$\frac{\partial E_{tot}(\{\mathbf{R}_I + \mathbf{u}_I\}, \mathbf{E})}{\partial \mathbf{u}_{s,\alpha} \partial \mathbf{E}_\beta} = \sum_{\gamma,\delta} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} \frac{\partial E_{tot}(\{\{S, \mathbf{a}\}(\mathbf{R}_I + \mathbf{u}_I)\}, \mathbf{E}')}{\partial \mathbf{u}_{\bar{s},\gamma} \partial \mathbf{E}'_\delta}, \tag{3.39}$$

or equivalently

$$Z^*_{s,\alpha,\beta} = \sum_{\gamma,\delta} S^{-1}_{\alpha,\gamma} S^{-1}_{\beta,\delta} Z^*_{\bar{s},\gamma,\delta}. \tag{3.40}$$

Chapter 4

Symmetry with spinors

In this chapter we present the modifications of the previous considerantions needed to deal with spinor wavefunctions. Spinors can be used together with fully relativistic pseudopotentials to include the effects of spin-orbit coupling. In this case, we can distinguish calculations performed in presence of time-reversal symmetry (nonmagnetic material) or without time reversal symmetry (magnetic material). In the latter case there might be symmetry operations that belong to the solid space group only when coupled with time reversal. If this happens, half rotations of the point group require time reversal and half do not require it. We indicate with $\{\mathcal{T}S, \mathbf{a}\}$ an operation of the space group that requires time reversal.

In the context of spinors it is also useful to define for each symmetry operation (with or without time reversal), the operator $\tilde{S}$ defined as $\tilde{S} = S$ if S is a proper rotation or $\tilde{S} = IS$ if S is an improper rotation. Here I is the inversion operator. Therefore $\tilde{S}$ is always a proper rotation. The inversion operation is defined as $I\mathbf{r} = -\mathbf{r}$.

For each rotation matrix S, there is in spin space a 2×2 matrix that belongs to the $SU(2)$ group that we indicate with $U(\tilde{S})$ that acts on the spinor part of the wavefunctions. It depends only on $\tilde{S}$ since inversion does not affect the spin part of the wavefunctions. A proper rotation is characterized by the versor of the rotation axis $\mathbf{n}$ and the rotation angle θ and the operator $U(\tilde{S})$ can be written as:

$$U(\tilde{S}) = e^{-i\frac{\theta}{2}\boldsymbol{\sigma}\cdot\mathbf{n}}, \tag{4.1}$$

where $\boldsymbol{\sigma}$ are the Pauli matrices.

4.1 The Kohn and Sham wavefunctions

In the noncollinear case, the Kohn and Sham equations are

$$\sum_{\sigma'} H_{KS}^{\sigma,\sigma'}\psi_{\mathbf{k},n,\sigma'}(\mathbf{r}) = \epsilon_{\mathbf{k},n}\psi_{\mathbf{k},n,\sigma}(\mathbf{r}), \tag{4.2}$$

and the Kohn and Sham Hamiltonian is a 2×2 matrix acting on two component spinors:

$$\Psi_{\mathbf{k},n} = \begin{pmatrix} \psi_{\mathbf{k},n,\uparrow}(\mathbf{r}) \\ \psi_{\mathbf{k},n,\downarrow}(\mathbf{r}) \end{pmatrix}. \tag{4.3}$$

Each spinor component is a Bloch function that can be written as:

$$\psi_{\mathbf{k},n,\sigma}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k},n,\sigma}(\mathbf{r}), \tag{4.4}$$

where $u_{\mathbf{k},n,\sigma}(\mathbf{r})$ is lattice periodic.

The operator $\mathcal{T}$ that applies time reversal to these spinors is an antilinear operator that can be written as:

$$\mathcal{T} = i\sigma_y \mathcal{K}, \tag{4.5}$$

where σ_y is the Pauli matrix:

$$\sigma_y = \begin{pmatrix} 0, & -i \\ i, & 0 \end{pmatrix} \tag{4.6}$$

and $\mathcal{K}$ is the complex conjugation operator. We have therefore:

$$\mathcal{T}\Psi_{\mathbf{k},n} = \begin{pmatrix} \psi^*_{\mathbf{k},n,\downarrow}(\mathbf{r}) \\ -\psi^*_{\mathbf{k},n,\uparrow}(\mathbf{r}) \end{pmatrix}. \tag{4.7}$$

and this is a Bloch function with wave-vector $-\mathbf{k}$. If the Hamiltonian is time reversal invariant, it commutes with $\mathcal{T}$ and $\mathcal{T}\Psi_{\mathbf{k},n}$ is also an eigenfunction of the Hamiltonian with the same eigenvalue $\epsilon_{\mathbf{k},n}$. We can call it $\Psi_{-\mathbf{k},n}$.

For each element of the space group $\{S, \mathbf{a}\}$ there will be an operator $O_{\{S,\mathbf{a}\}}$ that acts on the spinor wavefunctions as:

$$\left(O_{\{S,\mathbf{a}\}}\Psi_{\mathbf{k},n}\right)_\sigma = \sum_{\sigma'} U(\tilde{S})_{\sigma,\sigma'} \psi_{\mathbf{k},n,\sigma'}(\{S,\mathbf{a}\}^{-1}\mathbf{r}). \tag{4.8}$$

4.2 Charge and magnetization density

When the wavefunctions are spinors, the charge density is:

$$n(\mathbf{r}) = \sum_{\mathbf{k},v,\sigma} |\psi_{\mathbf{k},v,\sigma}(\mathbf{r})|^2, \tag{4.9}$$

One can demonstrate [2] that when we rotate the system with the operation $\{S, \mathbf{a}\}$ or with the operation $\{\mathcal{T}S, \mathbf{a}\}$ the charge density satisfies the same relation as in Eq. 2.12:

$$n(\mathbf{r}) = \frac{1}{N_S} \sum_{i=1}^{N_S} \tilde{n}(\{S_i, \mathbf{f}_i\}^{-1}\mathbf{r}). \tag{4.10}$$

For the magnetization density defined as

$$\mathbf{m}_\alpha(\mathbf{r}) = \mu_B \sum_{\mathbf{k},v,\sigma,\sigma'} \psi_{\mathbf{k},v,\sigma}(\mathbf{r})^* \boldsymbol{\sigma}_\alpha^{\sigma,\sigma'} \psi_{\mathbf{k},v,\sigma'}(\mathbf{r}), \tag{4.11}$$

where μ_B is the Bohr magneton, one has

$$\mathbf{m}_\alpha(\mathbf{r}) = \frac{1}{N_S} \sum_{i=1}^{N_S} (-1)^{T_{S_i}} \tilde{S}_{i,\alpha,\beta} \tilde{\mathbf{m}}_\beta(\{S_i, \mathbf{f}_i\}^{-1}\mathbf{r}), \tag{4.12}$$

where $\tilde{S}_i$ has been defined above and $T_{S_i} = 1$ if the operation needs time reversal and $T_{S_i} = 0$ otherwise.

We note that to calculate $\tilde{\mathbf{m}}_\beta(\mathbf{r})$ we must sum over the k points belonging to the irreducible Brillouin zone. This zone is found noting that for operations that require time reversal:

$$\mathcal{T}S\mathbf{k} = -S\mathbf{k}. \tag{4.13}$$

4.3 Forces and stress

No change is made in the symmetrization expression for forces and stress due to the time reversal operator since only the spatial part of the symmetry is used to rotate the atomic displacements and the strain.

4.4 Dynamical matrix

Eq. 3.11 is still valid both for operations that require time reversal and for those that do not require it:

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma}S^{-1}_{i,\beta,\delta}e^{iS_i\mathbf{q}\cdot\mathbf{R}^{S_i}_{\boldsymbol{\tau}_s}}\tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(S_i\mathbf{q})e^{-iS\mathbf{q}\cdot\mathbf{R}^{S_i}_{\boldsymbol{\tau}_{s'}}}. \tag{4.14}$$

We use these relations only for symmetries that belong to the small cogroup of $\mathbf{q}$:

$$S\mathbf{q} = \mathbf{q} + \mathbf{G}_S \tag{4.15}$$

if they do not require time reversal, or for which

$$S\mathbf{q} = -\mathbf{q} + \mathbf{G}_S \tag{4.16}$$

if they require time reversal. Introducing the operator $O(S_i) = \mathcal{K}$ if the operation is $\{\mathcal{T}S_i, \mathbf{a}_i\}$ or $O(S_i) = \mathbb{I}$ if the operation does not require time reversal, we can write

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{\gamma,\delta=1}^{3} S^{-1}_{i,\alpha,\gamma}S^{-1}_{i,\beta,\delta}O(S_i)\left[e^{i\mathbf{q}\cdot\mathbf{R}^{S_i}_{\boldsymbol{\tau}_s}}\tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}^{S_i}_{\boldsymbol{\tau}_{s'}}}\right], \tag{4.17}$$

where we used the fact that

$$\tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(-\mathbf{q}) = \tilde{D}^*_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q}). \tag{4.18}$$

Finally, in order to apply Eq. 3.10 we must recognize that for operations that require time reversal it actually reads:

$$D^*_{\bar{s},\alpha,\bar{s}',\beta}(S\mathbf{q}) = \sum_{\gamma,\delta=1}^{3} S_{i,\alpha,\gamma}S_{i,\beta,\delta}e^{-i\mathbf{q}\cdot\mathbf{R}^{S}_{\boldsymbol{\tau}_s}}D_{s,\gamma,s',\delta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}^{S}_{\boldsymbol{\tau}_{s'}}}, \tag{4.19}$$

What written here (and in particular Eq. 4.18) is valid for the adiabatic dynamical matrix at zero frequency. For magnetic material however a dynamical description (as well as possibly the coupling with magnons) for which Eq. 4.18 does not hold, is sometimes necessary to recover the experimental symmetries of the phonon modes.

4.5 Charge density and magnetization induced by a phonon

Eq. 3.25 that gives the charge induced by a phonon after an operation of the solid space group is still valid also if the operation requires time reversal. We have:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}e^{iS\mathbf{q}\cdot\{S,\mathbf{a}\}\mathbf{r}}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(S\mathbf{q})}e^{-iS\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}e^{-iS\mathbf{q}\cdot\mathbf{a}}, \tag{4.20}$$

For the practical implementation we choose to symmetrize only with operations $\{S,\mathbf{a}\}$ for which

$$S\mathbf{q}=\mathbf{q}+\mathbf{G}_S. \tag{4.21}$$

and with operations $\{\mathcal{T}S,\mathbf{a}\}$ for which

$$S\mathbf{q}=-\mathbf{q}+\mathbf{G}_S. \tag{4.22}$$

For the former one obtains the Eq. 3.29, while for the later we have

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}e^{iS\mathbf{q}\cdot\mathbf{a}}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(S\mathbf{q})}e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}e^{i\mathbf{q}\cdot\mathbf{a}}. \tag{4.23}$$

Now using the fact that

$$\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\bar{s},\beta}(-\mathbf{q}+\mathbf{G}_S)}=e^{-i\mathbf{G}_S\cdot(S\mathbf{r}+\mathbf{a})}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{\bar{s},\beta}(-\mathbf{q})}. \tag{4.24}$$

we have

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{-iS^{-1}\mathbf{G}_S\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(-\mathbf{q})}e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}. \tag{4.25}$$

This equation can be written also as:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}=e^{-i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{\beta=1}^{3}S^{-1}_{\alpha,\beta}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(-\mathbf{q})}e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}. \tag{4.26}$$

using the fact that $S^{-1}\mathbf{G}_S = \mathbf{G}_{S^{-1}}$ as can be deduced comparing the two expressions:

$$\begin{aligned} S\mathbf{q} &= -\mathbf{q} + \mathbf{G}_S \\ S^{-1}\mathbf{q} &= -\mathbf{q} + \mathbf{G}_{S^{-1}} \end{aligned} \tag{4.27}$$

after applying S^{-1} to the first. Note that if the operation requires time reversal, also its inverse requires it. Eqs. 3.29 and 4.26 can be summarized with the expression:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} = O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{\beta=1}^{3} S^{-1}_{\alpha,\beta}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}\right]. \tag{4.28}$$

This equation is further transformed before implementation (see the appendix on `irrep`).

Reasoning in the same manner, starting from Eq. 4.12 for the magnetization density, we obtain the equation

$$\frac{d\tilde{\mathbf{m}}_\gamma\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} = (-1)^{T_S}O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{\beta,\delta=1}^{3}\tilde{S}^{-1}_{\gamma,\delta}S^{-1}_{\alpha,\beta}\frac{d\tilde{\mathbf{m}}_\delta\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}\right]. \tag{4.29}$$

This equation is further transformed before implementation (see the appendix on `irrep`).

4.6 Dielectric constant and Born effective charges

No change is made in the symmetrization expression for dielectric constants and Born effective charges due to the time reversal operator since only the spatial part of the symmetry is used to rotate the displacements and the electric field.

Chapter 5

Appendices

The main symmetry variables available in Quantum ESPRESSO and their relationship with the symbol used in these notes are:

- `at(3,3)` contains the principal lattice vectors $\mathbf{a}_{\alpha,i}$ with this order for the two indices (the first is cartesian, the second indicates the vector).
- `bg(3,3)` contains the principal reciprocal lattice vectors $\mathbf{b}_{\alpha,i}$ with this order for the two indices (the first is cartesian, the second indicates the vector).
- `nsym` is N_S the number of symmetry operations of the point group.
- `s(3,3,48)` contains $S_{i,l,m}$. The symmetry index i is the third, while l, m are the first two indices.
- `sr(3,3,48)` contains $S_{i,\alpha,\beta}$, the rotation matrices in Cartesian coordinates.
- `ft(3,48)` contains $-\mathbf{f}_i$ the fractional translation with the negative sign. It is in crystal coordinates of the principal lattice vector. The symmetry index i is the second.
- `invs(48)` for each symmetry i gives the index of the inverse of S_i.
- `irt(48,nat)` for each atom s and symmetry i gives the index of the atom $\bar{s}$.
- `nsymq` is $N_{S_\mathbf{q}}$ the number of symmetry operations of the point cogroup of the $\mathbf{q}$ point.
- `rtau(3,48,nat)` contains $\mathbf{R}_{\boldsymbol{\tau}_s}^{S_i}$ (see Eq. 3.8) in Cartesian coordinates.
- `gi(3,48)` The vector $\mathbf{G}_{S_i^{-1}}$ associated to each symmetry $S_i^{-1}\mathbf{q} = \mathbf{q} + \mathbf{G}_{S_i^{-1}}$.
- `t_rev(48)` Contains T_{S_i}. For each symmetry operation it is equal to 1 if the symmetry requires time reversal, zero otherwise (used only in the noncollinear magnetic case).

- `u(3*nat,3*nat)` contains the displacements of each ($A^p_{s,\alpha}$). The second index is the index p of the different modes of the `irrep`, while the first is the composite index s, α.
- `t(npertx,npertx,48,3*nat)` contains the rotation matrices in the basis of the modes $t^S_{q,p}$. `npertx` is the maximum number of perturbations in a single `irrep`. The last index labels the `irreps`.
- `tmq(npertx,npertx,3*nat)` contains the rotation matrix S_m that sends $\mathbf{q}$ in $-\mathbf{q}+\mathbf{G}_{S_m}$ in the basis of the modes $t^{S_m}_{q,p}$.

5.1 Appendix: Symvector

This routine should apply Eq. 2.33. It actually calculates

$$\mathbf{F}_{s,\alpha} = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{\beta,\delta,\epsilon,l,m} \mathbf{b}_{\alpha,l}\mathbf{a}_{\epsilon,l}S^{-1}_{i,\epsilon,\beta}\mathbf{b}_{\beta,m}\mathbf{a}_{\delta,m}\mathbf{F}_{\bar{s},\delta}, \tag{5.1}$$

obtained introducing two delta functions in Eq. 2.33. The sum on δ in the last two terms gives the unsymmetrized forces in the basis of the reciprocal primitive vectors $\mathbf{F}_{\bar{s},m}$ and using Eq. 1.13 to make the sum over β and ϵ we can write

$$\mathbf{F}_{s,\alpha} = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{l,m} \mathbf{b}_{\alpha,l}S_{i,l,m}\mathbf{F}_{\bar{s},m}, \tag{5.2}$$

which is the expression implemented in this routine.

5.2 Appendix: Symmatrix

This routine symmetrizes 3×3 matrices such as the stress or the dielectric constants. These two quantities can be symmetrized with the same formula (see Eq. 2.40 and 3.36). We write the espression for stress:

$$\sigma_{\alpha,\beta} = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{\gamma,\delta,\epsilon,\eta,\nu,\rho}\sum_{l,m,n,p} \mathbf{b}_{\alpha,l}\mathbf{a}_{\epsilon,l}S^{-1}_{i,\epsilon,\eta}\mathbf{b}_{\eta,m}\mathbf{a}_{\gamma,m}\mathbf{b}_{\beta,n}\mathbf{a}_{\nu,n}S^{-1}_{i,\nu,\rho}\mathbf{b}_{\rho,p}\mathbf{a}_{\delta,p}\sigma_{\gamma,\delta}. \tag{5.3}$$

The sum over γ and δ give the stress in the basis of the primitive reciprocal vectors

$$\sigma_{m,p} = \sum_{\gamma,\delta=1}^{3} \mathbf{a}_{\gamma,m}\mathbf{a}_{\delta,p}\sigma_{\gamma,\delta}, \tag{5.4}$$

and Eq. 1.13 used twice to do the sums over ϵ, η, ν and ρ gives

$$\sigma_{\alpha,\beta} = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{l,m,n,p} \mathbf{b}_{\alpha,l}\mathbf{b}_{\beta,n}S_{i,l,m}S_{i,n,p}\sigma_{m,p}. \tag{5.5}$$

5.3 Appendix: Symtensor

With the same logic seen for the two previous routines, we find the expression used for symmetrizing the Born effective charges by this routine

$$Z^*_{s,\alpha,\beta} = \frac{1}{N_S}\sum_{i=1}^{N_S}\sum_{l,m,n,p} \mathbf{b}_{\alpha,l}\mathbf{b}_{\beta,n}S_{i,l,m}S_{i,n,p}Z^*_{\bar{s},m,p}, \tag{5.6}$$

where

$$Z^*_{\bar{s},m,p} = \sum_{\gamma,\delta=1}^{3} \mathbf{a}_{\gamma,m}\mathbf{a}_{\delta,p}Z^*_{\bar{s},\gamma,\delta} \tag{5.7}$$

is the Born effective charge written in the basis of the primitive reciprocal lattice vectors.

5.4 Appendix: Crys_to_cart

This routine receives a rank-two tensor in Cartesian coordinates and transforms it into a tensor in the basis of the primitive reciprocal vectors. It implements the Eq. 5.4:

$$\sigma_{m,p} = \sum_{\gamma,\delta=1}^{3} \mathbf{a}_{\gamma,m}\mathbf{a}_{\delta,p}\sigma_{\gamma,\delta}. \tag{5.8}$$

5.5 Appendix: Cart_to_crys

This routine receives a rank-two tensor in the basis of the primitive reciprocal lattice and transforms it into a tensor in Cartesian coordinates. It implements the equation:

$$\sigma_{\alpha,\beta} = \sum_{m,p=1}^{3} \mathbf{b}_{\alpha,m}\mathbf{b}_{\beta,p}\sigma_{m,p}. \tag{5.9}$$

5.6 Appendix: Rotate_grid_point

This routine receives the three integers `(i,j,k)` that represent the point:

$$\mathbf{r}_{i,j,k} = \frac{(i-1)}{N_1}\mathbf{a}_1 + \frac{(j-1)}{N_2}\mathbf{a}_2 + \frac{(k-1)}{N_3}\mathbf{a}_3, \tag{5.10}$$

where N_1, N_2, and N_3 are the sizes of the FFT mesh and gives as output the three integers `(ri,rj,rk)` that represent the point $\mathbf{r}'_{ri,rj,rk} = S\mathbf{r}_{i,j,k} + \mathbf{f}$ with

$$\mathbf{r}'_{ri,rj,rk} = \frac{(ri-1)}{N_1}\mathbf{a}_1 + \frac{(rj-1)}{N_2}\mathbf{a}_2 + \frac{(rk-1)}{N_3}\mathbf{a}_3. \tag{5.11}$$

Using Eq. 1.19, we obtain:

$$\begin{aligned}
\frac{(ri-1)}{N_1} &= S_{1,1}\frac{(i-1)}{N_1} + S_{2,1}\frac{(j-1)}{N_2} + S_{3,1}\frac{(k-1)}{N_3} + \mathbf{f}_1, \\
\frac{(rj-1)}{N_2} &= S_{1,2}\frac{(i-1)}{N_1} + S_{2,2}\frac{(j-1)}{N_2} + S_{3,2}\frac{(k-1)}{N_3} + \mathbf{f}_2, \\
\frac{(rk-1)}{N_3} &= S_{1,3}\frac{(i-1)}{N_1} + S_{2,3}\frac{(j-1)}{N_2} + S_{3,3}\frac{(k-1)}{N_3} + \mathbf{f}_3,
\end{aligned} \tag{5.12}$$

which can be rewritten as

$$\begin{aligned}
ri-1 &= S_{1,1}(i-1) + \frac{S_{2,1}N_1}{N_2}(j-1) + \frac{S_{3,1}N_1}{N_3}(k-1) + \mathbf{f}_1 N_1, \\
rj-1 &= \frac{S_{1,2}N_2}{N_1}(i-1) + S_{2,2}(j-1) + \frac{S_{3,2}N_2}{N_3}(k-1) + \mathbf{f}_2 N_2, \\
rk-1 &= \frac{S_{1,3}N_3}{N_1}(i-1) + \frac{S_{2,3}N_3}{N_2}(j-1) + S_{3,3}(k-1) + \mathbf{f}_3 N_3.
\end{aligned} \tag{5.13}$$

The routine `scale_sym_ops` updates the coefficients of the matrix S which are given in input to this routine.

5.7 Appendix: Sym_rho_serial

This routine first applies Eq. 2.25 to save in `rhosum` the symmetrized charge density, and then uses Eq. 2.28 to distribute the results to all the components $S_i\mathbf{G}$. $\mathbf{G}$ is transformed in the basis of the principal reciprocal lattice vectors and it is rotated with Eq. 1.28, so actually the rotation `ns` is applied not its inverse. `ft` is transformed in crystal coordinates at the beginning of the routine and the vector $S_i\mathbf{G}$ is actually `g_(:,igs)`. Note also that `ft` contains $-\mathbf{f}_i$ so the applied phase is actually $e^{iS_i\mathbf{G}\cdot\mathbf{f}}$ as written in Eq. 2.25.

5.8 Appendix: Coset

Let's give a few definitions. Given a group $G = \{g_1, g_2, ..., g_h\}$ with h elements, we call a subgroup $H = \{h_1, ..., h_k\}$ a subset of the elements of the group G that are still a group. If k is the number of elements of H, one can show that $N_c = h/k$ is an integer. Given H, we can define a left coset of G by chosing an element of G that does not belong to H, let's say g_i, and forming all the products $g_iH = \{g_ih_1, ..., g_ih_k\}$. This set is composed by k elements of G and is called a left coset. H and g_iH have no common elements, so we can write $G = H + g_iH + ...$ If $h/k = 2$ then $G = H + g_iH$ and we have finished, otherwise we can chose a g_j not contained in $H + g_iH$ and form another left coset g_jH. We continue in this way for N_c times and finally write $G = H + g_iH + g_jH + ...$

The routine coset gives and integer array `irg` of size h (called `nrot` inside the routine). The first k elements (called `nsym`) of `irg` give the elements of

H, then the next k elements are the indices of the first coset g_iH, the next k elements are the indices of the second coset g_jH, and so on.

In input the routine receives a logical array `sym` of size h such that `sym(l)` is `.TRUE.` if g_l belongs to H, and the multiplication table of the group G: $t(g_i, g_j)$, where $g_ig_j = g_{t(g_i,g_j)}$.

5.9 Appendix: Kpoint_grid

This routine generates a mesh of $N_1 \times N_2 \times N_3$ k points given N_1 (called `nk1`), N_2 (called `nk2`) and N_3 (called `nk3`) as:

$$\mathbf{k}_{ijk} = \left[\frac{(i-1)}{N_1} + \frac{k_1}{2N_1}\right]\mathbf{b}_1 + \left[\frac{(j-1)}{N_2} + \frac{k_2}{2N_2}\right]\mathbf{b}_2 + \left[\frac{(k-1)}{N_3} + \frac{k_3}{2N_3}\right]\mathbf{b}_3 \qquad (5.14)$$

where $1 \le i \le N_1$, $1 \le j \le N_2$, $1 \le k \le N_3$ and k_1, k_2 and k_3 are 0 or 1. At a generic iteration, the routine takes the first $\mathbf{k}_i$ in the list not already found in previous iterations and rotates it with all operations of the point group G of the Bravais lattice. If the rotated point is in the original list, it is removed and the weight of the point $\mathbf{k}_i$ is increased by 1. In output for each star of $\mathbf{k}_i$ (for G) we have only one point and its weight is the number of points of the star of $\mathbf{k}_i$ which were in the original grid. So the total weight is $N_1N_2N_3$. The weight are finally normalized so as to have sum 1.

5.10 Appendix: Irrek

This routine receives a list of k points (`nks` points) $\{\mathbf{k}_1, \mathbf{k}_2, ..., \mathbf{k}_N\}$ with their weights $\{w_1, ..., w_N\}$ that have been reduced by a point group G with h (`nrot`) elements, for instance those produced by the `kpoint_grid` routine. Given a subgroup H of G with k (`nsym`) elements, it gives the k points and their weights reduced with the group H.

The algorithm is the following: given $\mathbf{k}_i$ we rotate it with all elements of G and obtain the star of $\mathbf{k}_i$ (for G). Given $\mathbf{k}_i$ rotating with all elements of H we obtain the star of $\mathbf{k}_i$ for H. Of this star we have to save only the point $\mathbf{k}_i$. Let's consider now a generic coset g_lH and let's apply all its elements to $\mathbf{k}_i$. This gives the point $g_l\mathbf{k}_i$ and its star for H. Now if the point $g_l\mathbf{k}_i$ is not contained in all previous stars, we have to add $g_l\mathbf{k}_i$ to the list k. If it is contained in the star of $g_j\mathbf{k}_i$ we have to account that the coset g_jH has an additional star. The weight of each new $g_l\mathbf{k}_i$ will be the weight of $\mathbf{k}_i$ when reduced with G, divided by the number of cosets and multiplied by the number of stars equivalent to $g_l\mathbf{k}_i$.

5.11 Appendix: The irrep

In the phonon code we do not calculate derivatives of the charge density with respect to $\mathbf{u}_{s,\alpha}(\mathbf{q})$, but linear combinations of these derivatives that transform

as irreducible representations of the small space group of $\mathbf{q}$.

Suppose these linear combinations are given by $3 \times N_{at}$ vectors $A^p_{s,\alpha}$, where $1 \leq p \leq 3 \times N_{at}$. These vectors are obtained in the code as eigenvectors of a random matrix which is symmetrized as the dynamical matrix according to Eq. 3.13. These vectors are orthogonal, form a complete set, and are a basis for irreducible representations of the small co-group of $\mathbf{q}$. Orthogonality means that

$$\sum_{s,\alpha} A^{*,p}_{s,\alpha} A^q_{s,\alpha} = \delta^{p,q}. \tag{5.15}$$

Completeness means that

$$\sum_{p} A^p_{s,\alpha} A^{*,p}_{s',\beta} = \delta_{s,s'}\delta_{\alpha,\beta}. \tag{5.16}$$

Making linear combinations of Eq. 3.29 we get

$$\begin{aligned}\sum_{s,\alpha} A^p_{s,\alpha} \frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} &= e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}} \sum_{s,\alpha}\sum_{\beta=1}^{3} A^p_{s,\alpha} S^{-1}_{\alpha,\beta} \frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{\imath}}+\mathbf{u}_{\bar{\imath}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} \\ &= e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}} \sum_{q,s,\alpha,\bar{\bar{s}},\gamma,\beta} A^p_{s,\alpha} S^{-1}_{\alpha,\beta} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} A^{*,q}_{\bar{s},\beta} A^q_{\bar{\bar{s}},\gamma} \frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{\imath}}+\mathbf{u}_{\bar{\imath}}\}\right)}{d\mathbf{u}_{\bar{\bar{s}},\gamma}(\mathbf{q})}.\end{aligned} \tag{5.17}$$

Defining the charge induced by the irreducible mode λ^p as:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} = \sum_{s,\alpha} A^p_{s,\alpha} \frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})}, \tag{5.18}$$

the rotation matrix

$$t^S_{q,p} = \sum_{s,\alpha}\sum_{\beta=1}^{3} A^p_{s,\alpha} S^{-1}_{\alpha,\beta} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} A^{*,q}_{\bar{s},\beta} = \sum_{s,\alpha}\sum_{\beta=1}^{3} A^{*,q}_{\bar{s},\beta} S_{\beta,\alpha} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} A^p_{s,\alpha}, \tag{5.19}$$

we have the relationship:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} = e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}} \sum_{q} t^S_{q,p} \frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{\imath}}+\mathbf{u}_{\bar{\imath}}\}\right)}{d\lambda^q}. \tag{5.20}$$

This equation is implemented by summing on all symmetry operations of the small cogroup of $\mathbf{q}$ and dividing by their number:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} = \frac{1}{N_{S_\mathbf{q}}} \sum_{i=1}^{N_{S_\mathbf{q}}} e^{i\mathbf{G}_{S_i^{-1}}\cdot\mathbf{r}} \sum_{q} t^{S_i}_{q,p} \frac{d\tilde{n}\left(\{S_i,\mathbf{a}_i\}\mathbf{r},\{\mathbf{R}_{\bar{\imath}}+\mathbf{u}_{\bar{\imath}}\}\right)}{d\lambda^q}. \tag{5.21}$$

For operations that require the time reversal operators we must start by doing linear combinations of Eq. 4.28:

$$\begin{aligned}\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} &= \sum_{s,\alpha} A^p_{s,\alpha}\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} \\ &= O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{q,s,\alpha,\bar{\bar{s}},\gamma,\beta} A^{*p}_{s,\alpha}S^{-1}_{\alpha,\beta}A^{*q}_{\bar{s},\beta}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}A^q_{\bar{\bar{s}},\gamma}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\bar{s}},\gamma}(\mathbf{q})}\right].\end{aligned} \tag{5.22}$$

In this case we define

$$t^S_{q,p} = O(S)\left[\sum_{s,\alpha}\sum_{\beta=1}^{3} A^p_{s,\alpha}S^{-1}_{\alpha,\beta}e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}A^q_{\bar{s},\beta}\right] = O(S)\left[\sum_{s,\alpha}\sum_{\beta=1}^{3} A^q_{\bar{s},\beta}S_{\beta,\alpha}e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}A^p_{s,\alpha}\right], \tag{5.23}$$

and we have the relationship:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} = O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_q t^S_{q,p}\frac{d\tilde{n}\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\lambda^q}\right]. \tag{5.24}$$

Eq. 5.21 can be generalized in the noncolinear magnetic case as:

$$\frac{d\tilde{n}\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p} = \frac{1}{N_{S_\mathbf{q}}}\sum_{i=1}^{N_{S_\mathbf{q}}} O(S_i)\left[e^{i\mathbf{G}_{S_i^{-1}}\cdot\mathbf{r}}\sum_q t^{S_i}_{q,p}\frac{d\tilde{n}\left(\{S_i,\mathbf{a}_i\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\lambda^q}\right]. \tag{5.25}$$

where however we have two different definitions of $t^{S_i}_{q,p}$ Eq. 5.19 when time reversal is not needed and Eq. 5.23 when the symmetry operation needs time reversal.

Similar expressions can be be found for the symmetrization of the magnetization density. We need now to start from Eq. 4.29 and calculate the derivative of the magnetization with respect to the p irreducible mode. For operations that do not require time reversal we have:

$$\begin{aligned}\sum_{s,\alpha} A^p_{s,\alpha}\frac{d\tilde{\mathbf{m}}_\gamma\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} &= \left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{q,s,\alpha,\bar{\bar{s}},\beta,\delta,\eta} A^p_{s,\alpha}S^{-1}_{\alpha,\beta}A^{*q}_{\bar{\bar{s}},\beta}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}\right. \\ &\times \left. A^q_{\bar{\bar{s}},\eta}\tilde{S}^{-1}_{\gamma,\delta}\frac{d\tilde{\mathbf{m}}_\delta\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\bar{s}},\eta}(\mathbf{q})}\right].\end{aligned} \tag{5.26}$$

while for operations that require time reversal we have:

$$\begin{aligned}\sum_{s,\alpha} A^p_{s,\alpha}\frac{d\tilde{\mathbf{m}}_\gamma\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} &= (-1)^{T_S}O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{q,s,\alpha,\bar{\bar{s}},\beta,\delta,\eta} A^{*p}_{s,\alpha}S^{-1}_{\alpha,\beta}A^{*q}_{\bar{\bar{s}},\beta}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}}\right. \\ &\times \left. A^q_{\bar{\bar{s}},\eta}\tilde{S}^{-1}_{\gamma,\delta}\frac{d\tilde{\mathbf{m}}_\delta\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\bar{s}},\eta}(\mathbf{q})}\right].\end{aligned} \tag{5.27}$$

With the same definitions of $t^S_{q,p}$ used for the induced density we can summarize these two expressions with

$$\frac{d\tilde{\mathbf{m}}_\gamma\left(\mathbf{r},\{\mathbf{R}_I+\mathbf{u}_I\}\right)}{d\lambda^p}=(-1)^{T_S}O(S)\left[e^{i\mathbf{G}_{S^{-1}}\cdot\mathbf{r}}\sum_{q,\delta}t^S_{q,p}\tilde{S}^{-1}_{\gamma,\delta}\frac{d\tilde{\mathbf{m}}_\delta\left(\{S,\mathbf{a}\}\mathbf{r},\{\mathbf{R}_{\bar{I}}+\mathbf{u}_{\bar{I}}\}\right)}{d\lambda^q}\right]. \tag{5.28}$$

5.12 Appendix: Dynamical matrix in the basis of irrep

Given the eigenvalue equation that gives the phonon frequencies and the vibrational modes:

$$\sum_{s',\beta}D_{s,\alpha,s',\beta}(\mathbf{q})\mathbf{u}_{s',\beta}(\mathbf{q})=\omega^2(\mathbf{q})\mathbf{u}_{s,\alpha}(\mathbf{q}), \tag{5.29}$$

we can change the basis using the irrep. Multiplying the equation by $A^{*,p}_{s,\alpha}$ we get

$$\sum_q\sum_{s,\alpha}\sum_{s',\beta}\sum_{s'',\gamma}A^{*,p}_{s,\alpha}D_{s,\alpha,s',\beta}(\mathbf{q})A^q_{s',\beta}A^{*,q}_{s'',\gamma}\mathbf{u}_{s'',\gamma}(\mathbf{q})=\omega^2(\mathbf{q})\sum_{s,\alpha}A^{*,p}_{s,\alpha}\mathbf{u}_{s,\alpha}(\mathbf{q}), \tag{5.30}$$

and defining the dynamical matrix in the basis of the irrep:

$$D_{p,q}(\mathbf{q})=\sum_{s,\alpha}\sum_{s',\beta}A^{*,p}_{s,\alpha}D_{s,\alpha,s',\beta}(\mathbf{q})A^q_{s',\beta}, \tag{5.31}$$

and the new modes:

$$\mathbf{u}_q(\mathbf{q})=\sum_{s'',\gamma}A^{*,q}_{s'',\gamma}\mathbf{u}_{s'',\gamma}(\mathbf{q}), \tag{5.32}$$

the equation for phonon frequencies can be rewritten as:

$$\sum_q D_{p,q}(\mathbf{q})\mathbf{u}_q(\mathbf{q})=\omega^2(\mathbf{q})\mathbf{u}_p(\mathbf{q}). \tag{5.33}$$

We can also write the equation that transforms the dynamical matrix from the basis of the irrep to the Cartesian basis inverting Eq. 5.31:

$$D_{s,\alpha,s',\beta}(\mathbf{q})=\sum_{p,q}A^p_{s,\alpha}D_{p,q}(\mathbf{q})A^{*,q}_{s',\beta}. \tag{5.34}$$

5.13 Appendix: symdynph_gq

This routine uses the Eqs. 3.13 and 3.14 to symmetryze the dynamical matrix. We can rewrite Eq. 3.13 in the basis of the primitive reciprocal lattice vectors

inserting four δ in it:

$$\begin{aligned} D_{s,\alpha,s',\beta}(\mathbf{q}) &= \frac{1}{N_{S_\mathbf{q}}}\sum_{i=1}^{N_{S_\mathbf{q}}}\sum_{m,n,o,p}\sum_{\gamma,\delta,\eta,\lambda,\nu,\rho}\mathbf{b}_{\alpha,m}\mathbf{a}_{\eta,m}S_{i,\lambda,\eta}\mathbf{b}_{\lambda,n}\mathbf{a}_{\gamma,n}\mathbf{b}_{\beta,o}\mathbf{a}_{\nu,o}S_{i,\rho,\nu}\mathbf{b}_{\rho,p}\mathbf{a}_{\delta,p}\tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q})e^{i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)} \\ &= \frac{1}{N_{S_\mathbf{q}}}\sum_{i=1}^{N_{S_\mathbf{q}}}\sum_{m,n,o,p}\sum_{\gamma,\delta}\mathbf{b}_{\alpha,m}\mathbf{b}_{\beta,o}S_{i,m,n}S_{i,o,p}\mathbf{a}_{\gamma,n}\mathbf{a}_{\delta,p}\tilde{D}_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q})e^{i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)}. \end{aligned} \tag{5.35}$$

The routine receives as input the dynamical matrix in the basis of the primitive reciprocal lattice vectors:

$$\tilde{D}_{s,n,s',p}(\mathbf{q}) = \sum_{\gamma,\delta}\mathbf{a}_{\gamma,n}\mathbf{a}_{\delta,p}\tilde{D}_{s,\gamma,s',\delta}(\mathbf{q}), \tag{5.36}$$

computes

$$D_{s,m,s',o}(\mathbf{q}) = \frac{1}{N_{S_\mathbf{q}}}\sum_{i=1}^{N_{S_\mathbf{q}}}\sum_{n,p}S_{i,m,n}S_{i,o,p}\tilde{D}_{\bar{s},n,\bar{s}',p}(\mathbf{q})e^{i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)}. \tag{5.37}$$

This symmetrized dynamical matrix in the basis of the primitive reciprocal lattice vectors can be assigned to all elements $\bar{s},\bar{s}'$. To do this we can use Eq. 3.14 and write it in the basis of the primitive reciprocal lattice vectors:

$$\begin{aligned} D_{\bar{s},\alpha,\bar{s}',\beta}(\mathbf{q}) &= \sum_{m,n,o,p}\sum_{\gamma,\delta,\eta,\lambda,\nu,\rho}\mathbf{b}_{\alpha,m}\mathbf{a}_{\eta,m}S^{-1}_{i,\lambda,\eta}\mathbf{b}_{\lambda,n}\mathbf{a}_{\gamma,n}\mathbf{b}_{\beta,o}\mathbf{a}_{\nu,o}S^{-1}_{i,\rho,\nu}\mathbf{b}_{\rho,p}\mathbf{a}_{\delta,p}D_{s,\gamma,s',\delta}(\mathbf{q})e^{-i\mathbf{q}\cdot(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}})} \\ &= \sum_{m,n,o,p}\sum_{\gamma,\delta}\mathbf{b}_{\alpha,m}\mathbf{b}_{\beta,o}S^{-1}_{i,m,n}S^{-1}_{i,o,p}\mathbf{a}_{\gamma,n}\mathbf{a}_{\delta,p}D_{s,\gamma,s',\delta}(\mathbf{q})e^{-i\mathbf{q}\cdot(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}})}, \end{aligned} \tag{5.38}$$

or

$$D_{\bar{s},m,\bar{s}',o}(\mathbf{q}) = \sum_{n,p}S^{-1}_{i,m,n}S^{-1}_{i,o,p}D_{s,n,s',p}(\mathbf{q})e^{-i\mathbf{q}\cdot(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}})}. \tag{5.39}$$

On output the dynamical matrix is still in the basis of the primitive reciprocal lattice vectors and the sum over m,o in Eq. 5.38 that is needed to bring it in Cartesian coordinates is made outside this routine.

5.14 Appendix: $S_m\mathbf{q} = -\mathbf{q} + \mathbf{G}_m$

This option is used only with the collinear version of the code. It is disabled for spinors.

From the definition of the dynamical matrix (Eq. 3.1) we see that

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = D^*_{s,\alpha,s',\beta}(-\mathbf{q}). \tag{5.40}$$

If among the symmetry operations of the point group there is S_m such that

$$S_m\mathbf{q} = -\mathbf{q} + \mathbf{G}_{S_m} \tag{5.41}$$

we can use Eq. 3.9 to write

$$\begin{aligned} D_{s,\alpha,s',\beta}(\mathbf{q}) &= \sum_{\gamma,\delta=1}^{3} S^{-1}_{m,\alpha,\gamma} S^{-1}_{m,\beta,\delta} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} D_{\bar{s},\gamma,\bar{s}',\delta}(-\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}} \\ &= \left[\sum_{\gamma,\delta=1}^{3} S^{-1}_{m,\alpha,\gamma} S^{-1}_{m,\beta,\delta} e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} D_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}} \right]^* . \end{aligned} \tag{5.42}$$

So if we have a nonsymmetrized dynamical matrix we can use it with the equation

$$D_{s,\alpha,s',\beta}(\mathbf{q}) = \frac{1}{2} \left\{ D_{s,\alpha,s',\beta}(\mathbf{q}) + \left[\sum_{\gamma,\delta=1}^{3} S^{-1}_{m,\alpha,\gamma} S^{-1}_{m,\beta,\delta} e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} D_{\bar{s},\gamma,\bar{s}',\delta}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}} \right]^* \right\} \tag{5.43}$$

to symmetrize a dynamical matrix in which the matrix S_m has been used to reduce the $\mathbf{k}$ points.

A similar expression can be found also for charge density induced by a phonon. From the definition in Eq. 3.22 we have that:

$$\frac{dn\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(-\mathbf{q})} = \frac{dn\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)^*}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} \tag{5.44}$$

Now for the operation S_m in Eq. 5.41, Eq. 3.25 gives:

$$\begin{aligned} \frac{d\tilde{n}\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\mathbf{u}_{s,\alpha}(\mathbf{q})} &= e^{-i\mathbf{G}_{S_m^{-1}}\cdot\mathbf{r}} \sum_{\beta=1}^{3} S^{-1}_{m,\alpha,\beta} \frac{d\tilde{n}\left(\{S_m, \mathbf{a}_m\}\mathbf{r}, \{\mathbf{R}_{\bar{I}} + \mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(-\mathbf{q})} e^{i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} \\ &= \left[e^{i\mathbf{G}_{S_m^{-1}}\cdot\mathbf{r}} \sum_{\beta=1}^{3} S^{-1}_{m,\alpha,\beta} \frac{d\tilde{n}\left(\{S_m, \mathbf{a}_m\}\mathbf{r}, \{\mathbf{R}_{\bar{I}} + \mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{s},\beta}(\mathbf{q})} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} \right]^* \end{aligned} \tag{5.45}$$

Passing now to the basis of `irrep` we have that

$$\frac{d\tilde{n}\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\lambda_p} = \left[e^{i\mathbf{G}_{S_m^{-1}}\cdot\mathbf{r}} \sum_{q,s,\alpha,\bar{\bar{s}},\beta,\gamma} A^{*p}_{s,\alpha} S^{-1}_{m,\alpha,\beta} e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}_s}} A^{*q}_{\bar{s},\beta} A^{q}_{\bar{\bar{s}},\gamma} \frac{d\tilde{n}\left(\{S_m, \mathbf{a}_m\}\mathbf{r}, \{\mathbf{R}_{\bar{I}} + \mathbf{u}_{\bar{I}}\}\right)}{d\mathbf{u}_{\bar{\bar{s}},\gamma}(\mathbf{q})} \right]^* \tag{5.46}$$

Defining:

$$t^{S_m}_{q,p} = \left[\sum_{s,\alpha} \sum_{\beta=1}^{3} A^{p}_{s,\alpha} S^{-1}_{m,\alpha,\beta} e^{i\mathbf{q}\cdot\mathbf{R}^{S_m}_{\boldsymbol{\tau}_s}} A^{q}_{\bar{s},\beta} \right]^* = \left[\sum_{s,\alpha} \sum_{\beta=1}^{3} A^{q}_{\bar{s},\beta} S_{m,\beta,\alpha} e^{i\mathbf{q}\cdot\mathbf{R}^{S_m}_{\boldsymbol{\tau}_s}} A^{p}_{s,\alpha} \right]^* , \tag{5.47}$$

we obtain the equation:

$$\frac{d\tilde{n}\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\lambda_p} = \left[e^{i\mathbf{G}_{S_m^{-1}}\cdot\mathbf{r}} \sum_{q} t^{S_m}_{q,p} \frac{d\tilde{n}\left(\{S_m, \mathbf{a}_m\}\mathbf{r}, \{\mathbf{R}_{\bar{I}} + \mathbf{u}_{\bar{I}}\}\right)}{d\lambda_q} \right]^* , \tag{5.48}$$

that can be used in the symmetrization expression:

$$\frac{d\tilde{n}\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\lambda_p} = \frac{1}{2} \left\{ \frac{d\tilde{n}\left(\mathbf{r}, \{\mathbf{R}_I + \mathbf{u}_I\}\right)}{d\lambda_p} + \left[e^{i\mathbf{G}_{S_m^{-1}}\cdot\mathbf{r}} \sum_{q} t^{S_m}_{q,p} \frac{d\tilde{n}\left(\{S_m, \mathbf{a}_m\}\mathbf{r}, \{\mathbf{R}_{\bar{I}} + \mathbf{u}_{\bar{I}}\}\right)}{d\lambda_q} \right]^* \right\}, \tag{5.49}$$

5.15 Appendix: set_irr_sym

This routine implements the three Eqs. 5.23, 5.19, and 5.47. In all cases the matrix $S_{\beta,\alpha}$ is applied in the crystal basis. We show explicitly only the case of $t^S_{q,p}$. We have that using twice Eq. 1.11 we obtain:

$$\begin{aligned} t^S_{q,p} &= \sum_{s,\alpha,\beta,\delta,\eta,j,l} A^{*,q}_{\bar{s},\beta}\mathbf{b}_{\delta,j}\mathbf{a}_{\beta,j}S_{\delta,\alpha}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}s}}\mathbf{b}_{\eta,l}\mathbf{a}_{\alpha,l}A^p_{s,\eta} \\ &= \sum_{s,\alpha,\beta,\delta,\eta,j,l} A^{*,q}_{\bar{s},\beta}\mathbf{a}_{\beta,j}\mathbf{b}_{\delta,j}S_{\delta,\alpha}\mathbf{a}_{\alpha,l}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}s}}\mathbf{b}_{\eta,l}A^p_{s,\eta} \\ &= \sum_{s,\beta,j,l} A^{*,q}_{\bar{s},\beta}\mathbf{a}_{\beta,j}e^{-i\mathbf{q}\cdot\mathbf{R}^S_{\boldsymbol{\tau}s}}S_{l,j}A^p_{s,l}, \end{aligned} \tag{5.50}$$

where

$$A^p_{s,l} = \sum_{\eta}\mathbf{b}_{\eta,l}A^p_{s,\eta} \tag{5.51}$$

is the mode in the basis of the primitive lattice vectors.

5.16 Appendix: rotate_and_add_dyn

This routine implements Eq. 3.10 adding four δ functions:

$$\begin{aligned} D_{\bar{s},\alpha,\bar{s}',\beta}(S\mathbf{q}) &= \sum_{p,q,r,t,\gamma,\delta,\epsilon,\eta,\nu,\rho} \mathbf{b}_{\alpha,p}\mathbf{a}_{\eta,p}S_{\eta,\nu}\mathbf{b}_{\nu,q}\mathbf{a}_{\gamma,q}\mathbf{b}_{\beta,r}\mathbf{a}_{\rho,r}S_{\rho,\epsilon}\mathbf{b}_{\epsilon,t}\mathbf{a}_{\delta,t}D_{s,\gamma,s',\delta}(\mathbf{q})e^{-i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)} \\ &= \sum_{p,q,r,t,\gamma,\delta,\epsilon,\eta,\nu,\rho} \mathbf{b}_{\alpha,p}\mathbf{b}_{\beta,r}\mathbf{a}_{\eta,p}S^{-1}_{\nu,\eta}\mathbf{b}_{\nu,q}\mathbf{a}_{\rho,r}S^{-1}_{\epsilon,\rho}\mathbf{b}_{\epsilon,t}\mathbf{a}_{\gamma,q}\mathbf{a}_{\delta,t}D_{s,\gamma,s',\delta}(\mathbf{q})e^{-i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)} \\ &= \sum_{p,q,r,t} \mathbf{b}_{\alpha,p}\mathbf{b}_{\beta,r}S^{-1}_{p,q}S^{-1}_{r,t}D_{s,q,s',t}(\mathbf{q})e^{-i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)}, \end{aligned} \tag{5.52}$$

Where the dynamical matrix in the basis of the primitive lattice vectors is given as input to the routine:

$$D_{s,q,s',t}(\mathbf{q}) = \sum_{\gamma,\delta} \mathbf{a}_{\gamma,q}\mathbf{a}_{\delta,t}D_{s,\gamma,s',\delta}(\mathbf{q}) \tag{5.53}$$

and the output of the routine is the dynamical matrix at the rotated $\mathbf{q}$ in the same basis

$$D_{\bar{s},p,\bar{s}',r}(S\mathbf{q}) = \sum_{q,t} S^{-1}_{p,q}S^{-1}_{r,t}D_{s,q,s',t}(\mathbf{q})e^{-i\mathbf{q}\cdot\left(\mathbf{R}^S_{\boldsymbol{\tau}_s}-\mathbf{R}^S_{\boldsymbol{\tau}_{s'}}\right)} \tag{5.54}$$

The operations needed to pass to the Cartesian basis are made outside the routine if needed:

$$D_{s,\alpha,s',\beta}(S\mathbf{q}) = \sum_{p,r} \mathbf{b}_{\alpha,p}\mathbf{b}_{\beta,r}D_{s,p,s',r}(S\mathbf{q}) \tag{5.55}$$

Chapter 6

Bibliography

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