

## ELECTRONIC AND VIBRATIONAL STATES OF CRYSTALS

**(38) Schrödinger's Equation:** Electronic and vibrational states describe the characteristics of electronic distributions and atomic oscillations for molecules and solids. Electronic states are wavefunctions  $\Psi_{el}(\mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N)$  of the electronic spatial ( $\mathbf{r}_i$ ) and spin ( $\sigma_i$ ) coordinates. Vibrational states are wavefunctions  $\Psi_{vib}(\mathbf{u}_1, \dots, \mathbf{u}_N)$  of small displacements of atoms from their equilibrium positions ( $\mathbf{u}_i = \mathbf{R}_i - \mathbf{R}_{i0}$ ). These wavefunctions are eigenfunctions of the time-independent Schrödinger equation  $H\Psi = E\Psi$ , in which  $H$  is the Hamiltonian (energy operator) consisting of the sum of kinetic and potential energy operators acting on the wavefunction  $\Psi$ , and the eigenvalue  $E$  is the energy of the state  $\Psi$ . For the moment, we focus on electronic states and will briefly address vibrational states later.

Solving the Schrödinger equation for electronic states starts with the Born-Oppenheimer approximation and then involves methods such as Hartree-Fock techniques or density functional theory to address the challenges of electron-electron interactions. Many approaches yield effective one-electron wavefunctions or *orbitals*  $\psi_n(\mathbf{r})$ , which describe the spatial distribution of electrons. When spin-orbit coupling or the presence of any magnetic fields are neglected, electron spin doubles the degeneracy of every orbital. These one-electron wavefunctions are eigenfunctions of the *general* effective one-electron Schrödinger equation

$$H(\mathbf{r})\psi_n(\mathbf{r}) = (T(\mathbf{r}) + V(\mathbf{r}))\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}).$$

The energy operator  $H(\mathbf{r})$  depends on electronic position  $\mathbf{r}$  because expressions for the kinetic energy operator  $T(\mathbf{r})$  involves spatial second derivatives and the potential energy operator  $V(\mathbf{r})$  depends on electronic positions relative to the atomic nuclei. The orbitals  $\psi_n(\mathbf{r})$  and their corresponding energies  $E_n$  are labeled by quantum numbers  $n$  that depend on the symmetry and boundary conditions associated with the chemical structure. As eigenfunctions of  $H(\mathbf{r})$ , each orbital  $\psi_n(\mathbf{r})$  is normalized and two orbitals with different quantum numbers  $\psi_m(\mathbf{r})$  and  $\psi_n(\mathbf{r})$  are orthogonal:

$$\int \psi_m^*(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r} \equiv \langle \psi_m | \psi_n \rangle = \delta_{mn}, (\delta_{mn} = 1 \text{ if } m = n; \delta_{mn} = 0 \text{ if } m \neq n).$$

This integral defines the Dirac bra-ket notation. As a result, each eigenvalue is

$$E_n = \int \psi_n^*(\mathbf{r})H(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r} \equiv \langle \psi_n | H | \psi_n \rangle.$$

Moreover, each orbital yields a probability distribution of electron density  $\rho_n(\mathbf{r})$  given as

$$\rho_n(\mathbf{r}) = \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}).$$

At this point, *how do the symmetry operations of a point group or a space group affect the Schrödinger equation?* Since the Schrödinger equation is an equality between two scalar functions, consider how transformations affect scalar functions in general.

**TRANSFORMATIONS OF SCALAR FUNCTIONS:** Scalar functions have a definite numerical value  $\varphi(\mathbf{r})$  at every point  $\mathbf{r}$  in space, and that value is independent of any coordinate system. In a different coordinate system, the point  $\mathbf{r}$  will be expressed as  $\mathbf{r}'$  and the function will be expressed by  $\varphi'$ , but the scalar value  $\varphi'(\mathbf{r}')$  remains unchanged, i.e.,  $\varphi'(\mathbf{r}') = \varphi(\mathbf{r})$ .

Consider a transformation  $G$  that takes  $\mathbf{r}$  to  $\mathbf{r}'$ , i.e.,  $\mathbf{r}' = G\mathbf{r}$ . Then, the function  $\varphi$  transforms into the new function  $\varphi' = G\varphi$ , and

$$\varphi'(\mathbf{r}') = G\varphi(G\mathbf{r}) = \varphi(\mathbf{r}), \text{ or } G\varphi(\mathbf{r}) = \varphi(G^{-1}\mathbf{r}).$$

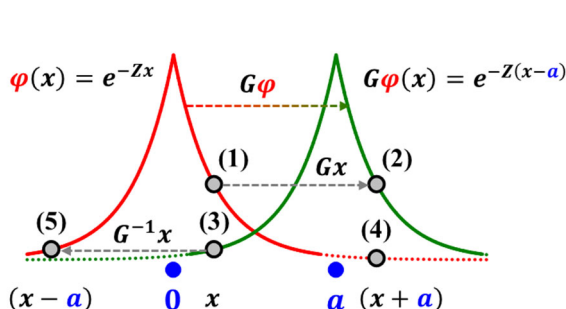
As a result, the expression for the new function  $\varphi' = G\varphi$  can be determined by evaluating the original function  $\varphi$  at  $G^{-1}\mathbf{r}$ .

**Example:** For  $\varphi(x) = e^{-Zx}$  and  $Gx = x + a$ , determine the expression for  $G\varphi(x)$ .

Since  $x = (GG^{-1})x = G(G^{-1}x) = G^{-1}x + a$ , then  $G^{-1}x = x - a$ .

Therefore,  $G\varphi(x) = \varphi(G^{-1}x) = \varphi(x - a) = e^{-Z(x-a)}$ .

The figure below illustrates this result:



**Red Curve:**  $\varphi(x) = e^{-Zx}$  around the origin.

**Green Curve:**  $G\varphi(x) = e^{-Z(x-a)}$  around  $a$ .

(1)  $\varphi(x)$

(2)  $G\varphi(Gx) = G\varphi(x + a) = \varphi(x)$

(3)  $G\varphi(x) \neq \varphi(x)$

(4)  $\varphi(Gx) = \varphi(x + a) \neq \varphi(x)$

(5)  $\varphi(G^{-1}x) = \varphi(x - a) = G\varphi(x)$

Now, consider a group of  $g$  operations  $\{E, G_2, \dots, G_g\}$  such that  $G_k = G_i G_j$ . This product operates right-to-left on coordinates, which means  $G_k \mathbf{r} = G_i G_j \mathbf{r} = G_i(G_j \mathbf{r})$ . To obtain the same product outcome when applied to functions, the product must operate as follows:

$$G_k \varphi(\mathbf{r}) = G_i G_j \varphi(\mathbf{r}) = G_i[G_j \varphi(\mathbf{r})] = G_j \varphi(G_i^{-1} \mathbf{r}) = \varphi(G_j^{-1} G_i^{-1} \mathbf{r}) = \varphi((G_i G_j)^{-1} \mathbf{r}) = \varphi(G_k^{-1} \mathbf{r}).$$

Returning to the effective one-electron Schrödinger equation, consider a transformation  $G$  acting on the function  $H(\mathbf{r})\psi_n(\mathbf{r})$ :

$$G[H(G\mathbf{r})\psi_n(G\mathbf{r})] = GH(G\mathbf{r})[G^{-1}\psi_n(\mathbf{r})] = [GH(G\mathbf{r})G^{-1}]\psi_n(\mathbf{r}) = H(\mathbf{r})\psi_n(\mathbf{r}).$$

If the operation  $G$  is a member of the space group for the crystalline structure being studied, then the one-electron Hamiltonian is invariant with respect to this transformation, i.e.,  $H(G\mathbf{r}) = H(\mathbf{r})$ . As a result,

$$GH(G\mathbf{r})G^{-1} = GH(\mathbf{r})G^{-1} = H(\mathbf{r}), \text{ or } GH(\mathbf{r}) = H(\mathbf{r})G,$$

i.e.,  $G$  commutes with  $H(\mathbf{r})$ . The set  $\mathcal{G}$  of all operations  $\{E, G_2, \dots, G_g\}$  that commute with  $H(\mathbf{r})$  forms a group called *the group of the Hamiltonian* or *the group of the Schrödinger equation*. These operations do not change the kinetic and potential energy operators. Since the potential energy operator depends on the atomic positions of the structure, then this set contains all operations that keep the structure invariant. Therefore, for a crystalline solid this set is the space group.

So, for  $\psi_n(\mathbf{r})$  an eigenfunction of  $H(\mathbf{r})$  with eigenvalue  $E_n$ , every transformed wavefunction  $G_j \psi_n(\mathbf{r})$  is also an eigenfunction of  $H(\mathbf{r})$  with the same eigenvalue  $E_n$ . Furthermore, the wavefunction  $\psi_n(\mathbf{r})$  is a basis function for an irreducible representation of the group  $\mathcal{G}$ . Now, there are two types of eigenfunctions of the Schrödinger equation to consider:

- $\psi_n(\mathbf{r})$  is NONDEGENERATE: Given the characteristics of eigenfunctions of the Schrödinger equation,  $G_j \psi_n(\mathbf{r})$  will differ from  $\psi_n(\mathbf{r})$  by at most a phase factor<sup>12</sup>, i.e.,

$$G_j \psi_n(\mathbf{r}) = \psi_n(G_j^{-1} \mathbf{r}) = e^{i\omega_j} \psi_n(\mathbf{r}) \equiv D^{(n)}(G_j) \psi_n(\mathbf{r}).$$

$D^{(n)}(G_j) = e^{i\omega_j}$  is a  $1 \times 1$  matrix representative of  $G_j$  when  $G_j$  operates on the normalized function  $\psi_n(\mathbf{r})$ . Applying a second operation  $G_i$  to  $G_j \psi_n(\mathbf{r})$  yields

$$G_i G_j \psi_n(\mathbf{r}) = e^{i\omega_i} e^{i\omega_j} \psi_n(\mathbf{r}) = D^{(n)}(G_i) D^{(n)}(G_j) \psi_n(\mathbf{r}).$$

<sup>12</sup> According to the postulates of quantum mechanics, the two functions  $\psi$  and  $e^{i\omega}\psi$  denote identical physical states.

If  $G_i G_j = G_k$ , then  $D^{(n)}(G_k) = e^{i\omega_k} = e^{i\omega_i} e^{i\omega_j} = D^{(n)}(G_i) D^{(n)}(G_j) = D^{(n)}(G_i G_j)$ .

Therefore, application of each group operation  $G_j$  to  $\psi_n(\mathbf{r})$  creates a 1-dimensional *irreducible representation*  $D^{(n)}$  of the group of the Hamiltonian  $\mathcal{G}$  with the eigenfunction  $\psi_n(\mathbf{r})$  serving as a basis function. Different nondegenerate eigenfunctions of  $H(\mathbf{r})$  can be basis functions for the same irreducible representation of the group  $\mathcal{G}$ .

- $\psi_n(\mathbf{r})$  is DEGENERATE: If  $\psi_n^{(l)}(\mathbf{r})$  is one of  $m$  degenerate eigenfunctions  $\psi_n^{(p)}(\mathbf{r})$ , ( $p = 1, \dots, m$ ), then  $G_j \psi_n^{(l)}(\mathbf{r})$  will be a linear combination of the entire set of  $m$  eigenfunctions:

$$G_j \psi_n^{(l)}(\mathbf{r}) = \sum_{p=1}^m [D^{(n)}(G_j)]_{pl} \psi_n^{(p)}(\mathbf{r}).$$

$D^{(n)}(G_j)$  is an  $m \times m$  matrix representative of operation  $G_j$  and  $[D^{(n)}(G_j)]_{pl}$  is the matrix element of the  $p^{\text{th}}$  row and the  $l^{\text{th}}$  column of this matrix. Applying  $G_i$  to  $G_j \psi_n^{(l)}(\mathbf{r})$  yields

$$\begin{aligned} G_i G_j \psi_n^{(l)}(\mathbf{r}) &= G_i \left( \sum_{r=1}^m [D^{(n)}(G_j)]_{rl} \psi_n^{(r)}(\mathbf{r}) \right) = \sum_{r=1}^m [D^{(n)}(G_j)]_{rl} G_i \psi_n^{(r)}(\mathbf{r}) \\ &= \sum_{r=1}^m [D^{(n)}(G_j)]_{rl} \left( \sum_{p=1}^m [D^{(n)}(G_i)]_{pr} \psi_n^{(p)}(\mathbf{r}) \right) \\ &= \sum_{r=1}^m \sum_{p=1}^m [D^{(n)}(G_i)]_{pr} [D^{(n)}(G_j)]_{rl} \psi_n^{(p)}(\mathbf{r}) \\ &= \sum_{p=1}^m \left( \sum_{r=1}^m [D^{(n)}(G_i)]_{pr} [D^{(n)}(G_j)]_{rl} \right) \psi_n^{(p)}(\mathbf{r}) \\ &= \sum_{p=1}^m [D^{(n)}(G_i G_j)]_{pl} \psi_n^{(p)}(\mathbf{r}). \end{aligned}$$

If  $G_i G_j = G_k$ , then  $D^{(n)}(G_k) = D^{(n)}(G_i G_j) = D^{(n)}(G_i) D^{(n)}(G_j)$ , so that  $D^{(n)}$  is an  $m$ -dimensional representation of the group  $\mathcal{G}$ . This representation is *irreducible*, unless the degeneracy is *accidental*, which means that not all symmetries of the problem have been properly identified.

**(39)** We can now make the following assertions regarding the symmetry of the Schrödinger equation for a crystalline solid adopting space group  $\mathcal{G} = \mathcal{R} \otimes \mathcal{L} = \{(R|\boldsymbol{\tau}_R)\} \otimes \{(1|\mathbf{T}_{mnp})\}$ :

- (a) The Hamiltonian  $H(\mathbf{r})$  is *invariant* for all operations of the space group. That is,  $H(\mathbf{r})$  is totally symmetric for the space group. Since the operations of the Bravais lattice  $\mathcal{L}$  form a subgroup of  $\mathcal{G}$ , then  $H(\mathbf{r})$  is also periodic in the Bravais lattice:

$$(1|\mathbf{T}_{mnp})H(\mathbf{r}) = H\left((1|\mathbf{T}_{mnp})^{-1}\mathbf{r}\right) = H(\mathbf{r} - \mathbf{T}_{mnp}) = H(\mathbf{r}).$$

By replacing  $\mathbf{r}$  with  $\mathbf{r} + \mathbf{T}_{mnp}$ , then

$$H(\mathbf{r} + \mathbf{T}_{mnp}) = H(\mathbf{r}).$$

- (b) The eigenvalues (energies)  $E_n$  are invariant for all operations of the space group because they are scalar values. The “quantum numbers”  $n$  serve as labels for the wavefunctions  $\psi_n(\mathbf{r})$ .
- (c) The eigenfunctions (orbitals)  $\psi_n(\mathbf{r})$  are basis functions for irreducible representations of the space group. Since  $\mathcal{L}$  is an invariant subgroup of  $\mathcal{G}$ , these representations can be built (“induced”) from the irreducible representations of the translational symmetry operations  $\mathcal{L}$ .

Therefore, before examining the irreducible representations of a space group, we start with irreducible representations of translational symmetry operations  $\mathcal{L}$ , which introduces the concept of reciprocal space or  $k$ -space.

REPRESENTATIONS: Symmetry operations are linear operators that transform sets of coordinates or functions of a vector space into new coordinates or new functions of the same vector space. To evaluate these changes, the symmetry operations are *represented* by square matrices, for which the number of rows or columns is the dimension of the *representation*. Since there are many possible vector spaces that can be used to describe atomic and electronic structure, there are several possible representations of symmetry groups. Most representations are *reducible*, which means that every matrix can be written in an equivalent block-diagonal form after a similarity transformation:<sup>13</sup>

$$D(R) = \begin{pmatrix} D^{(1)}(R) & 0 & \cdots & 0 \\ 0 & D^{(2)}(R) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & D^{(\mu)}(R) \end{pmatrix} \equiv D^{(1)}(R) \oplus D^{(2)}(R) \oplus \cdots \oplus D^{(\mu)}(R).$$

If a matrix representation cannot be transformed into block-diagonal form, then the representation is called *irreducible*. Irreducible representations (IRs) are the fundamental representations from which all reducible representations for a group can be composed. One-dimensional representations are scalars, and are necessarily irreducible. There are 1-, 2-, and 3-dimensional IRs among the crystallographic point groups, and the non-crystallographic icosahedral point groups  $\mathcal{I}$  and  $\mathcal{I}_h$  allow 4- and 5-dimensional IRs.

GREAT ORTHOGONALITY THEOREM (“GOT”): If  $D^{(i)}$  and  $D^{(j)}$  are two irreducible representations of a group  $\mathcal{G}$ , then this theorem provides the following relationships among the matrix elements of these two representations:

$$\sum_{R \in \mathcal{G}} [D^{(i)}(R)]_{\mu\nu}^* [D^{(j)}(R)]_{\mu'\nu'} = \frac{g}{l_i} \delta_{ij} \delta_{\mu\mu'} \delta_{\nu\nu'}.$$

In this equation,  $[D^{(i)}(R)]_{\mu\nu}$  is the matrix element of the  $\mu^{\text{th}}$  row and  $\nu^{\text{th}}$  column of the matrix representative  $D^{(i)}$  for the operation  $R$  of  $\mathcal{G}$ . The dimension of  $D^{(i)}$  is  $l_i$ . Given the equivalence of representations related to each other by a similarity transformation, this theorem can be revised to express relationships among the characters  $\chi^{(i)}(R)$  of IRs. Recall, the character of a representation for a specific group member is the trace of the corresponding matrix. Because the character is invariant under any similarity transformation, operations belonging to the same class of a group have the same character. Also, the dimension of a representation is the character of the identity operation. From the GOT, several important relationships involving characters can be deduced:

- Two equivalent representations have equal sets of characters;
- A representation is irreducible if and only if  $\sum_{R \in \mathcal{G}} |\chi(R)|^2 = g$ ;
- The number of times  $n_i$  that IR  $D^{(i)}$  occurs in the reduction of a reducible representation  $D$  is
 
$$n_i = \frac{1}{g} \sum_{R \in \mathcal{G}} \chi(R) \chi^{(i)}(R)^*;$$
- The number of IRs equals the number of classes in a group;
- The order of the group equals the sum of the squared dimensions of all IRs:  $g = \sum l_i^2$ ;
- The sum of characters of the entire group for different IRs are orthogonal:  $\sum_{R \in \mathcal{G}} \chi^{(i)}(R)^* \chi^{(j)}(R) = g \delta_{ij}$ ;
- The sum of characters for different classes over all IRs are orthogonal:  $\sum_i \chi^{(i)}(\mathcal{C}_k)^* \chi^{(i)}(\mathcal{C}_j) N_k = g \delta_{kj}$ , in which the sum is over all IRs and  $N_k$  = number of members in class  $\mathcal{C}_k$ .

The last four relationships provide the basis for constructing *character tables* for finite groups:

$\mathcal{G}$	$\mathcal{C}_1 = E$	$\cdots$	$\mathcal{C}_k$	$\cdots$	$\mathcal{C}_N$	Basis Function(s)
IR $D^{(1)}$	1	$\cdots$	1	$\cdots$	1	$\psi_1$ (1-d; Totally Symmetric IR)
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
IR $D^{(i)}$	$l_i$	$\cdots$	$\chi^{(i)}(\mathcal{C}_k)$	$\cdots$	$\chi^{(i)}(\mathcal{C}_N)$	$\psi_i$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
IR $D^{(N)}$	$l_N$	$\cdots$	$\chi^{(N)}(\mathcal{C}_k)$	$\cdots$	$\chi^{(N)}(\mathcal{C}_N)$	$\psi_N$

<sup>13</sup> The symbol “D” stands for the German word *Darstellung*, which means “representation”.