Chapter 5
What has Quantum Chemistry Got to Do with It?

Abstract The time has come to see how the concept of irreducible representations ties in with quantum chemistry. After a brief introduction to the prequantum principles of symmetry, we will show that eigenfunctions of the Hamiltonian are also eigenfunctions of the symmetry operators that commute with the Hamiltonian. We further analyze the concept of a degeneracy and show how the degenerate components can be characterized by canonical symmetry relationships. The final section will then provide a detailed account of the symmetry operations that leave the Hamiltonian invariant.

Contents

5.1 The Prequantum Era

Nature around us is full of disorder and chaos, yet it also offers intriguing examples of perfect order and symmetry. Ever since prehistoric times, man has been admiring the circular geometry of a full moon or the perfectly flat surface of a calm sea. Crystals offer another example of almost ideal symmetrical shapes, and it is no surprise that early recognition of the important role of symmetry in physics was based on the study of properties of crystals. Two pioneers of the prequantum era, Franz Neumann and Pierre Curie [1], stand out for their important conjectures.

Theorem 9 *Neumann's principle states that the symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal.*

We can apply this directly to a molecule such as ammonia. Ammonia carries a permanent dipole moment, μ_z, which is oriented along the threefold axis. In-plane

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components of the dipole moment are strictly forbidden. This is in agreement with the Neumann principle. A dipole moment corresponds to a displacement of charge, and the only displacement that does not destroy the molecular point group is along the z-direction. Hence, this is the only direction that is compatible with the Neumann principle.

Pierre Curie realized that this principle is not limited to crystals, but applies to physical phenomena in general, and not only to isolated systems, but also to systems subject to external perturbations. His proposition is known as the principle of *dissymmetry*.

Theorem 10 *The symmetry of a phenomenon is the maximal symmetry compatible with the existence of the phenomenon. In order for a phenomenon to exist, it is necessary that certain elements of symmetry are absent: dissymmetry creates the phenomenon.*

Curie understood that under stress, or in the presence of external electric or magnetic fields, the symmetry of a system is changed. The Neumann principle still applies but should no longer be based on the symmetry of the isolated crystal, but on that of the combined system of crystal and external field, as we have considered in Sect. 3.9. In the case of ammonia, application of an electric field has the $C_{\infty v}$ symmetry of a polar vector. The symmetry that results from the superposition of the field with the molecular point group C_{3v} depends on the orientation (see Appendix B). In the coordinate frame of Fig. 3.1 one has:

$$\begin{aligned} z &: C_{\infty v} \cap C_{3v} = C_{3v} \\ x &: C_{\infty v} \cap C_{3v} = C_s \\ y &: C_{\infty v} \cap C_{3v} = C_1 \end{aligned} \tag{5.1}$$

If the field is oriented along the z-direction, it will keep the C_{3v} symmetry of the molecule. This is also in line with the existence of a permanent dipole in the z-direction according to the Neumann principle since a charge dipole has the same symmetry as an electric field. If an external field is applied in the x-direction, the symmetry is reduced to the reflection group, $C_s = \{\hat{E}, \hat{\sigma}_1\}$. In the presence of such a field, displacement of charge in the x-direction is compatible with the extended symmetry principle, which means that ammonia can acquire an *induced* dipole moment in the x-direction. However, a field along x cannot induce a dipole moment in the y-direction since the σ_1 reflection plane is incompatible with the displacement of charge across the plane of symmetry.

The symmetry principles of Neumann and Curie can be recast in the language of irreducible representations. The requirement that physical properties be invariant under the symmetry elements of the point group simply means that they should transform as the totally symmetric irrep. For the dipole moment, the components

transform as follows:

$$\begin{aligned} \Gamma(\mu_z) &= a_1 \\ \Gamma(\mu_x, \mu_y) &= e \end{aligned} \tag{5.2}$$

Hence, only the z-component is compatible with the existence of a dipole moment.

The principles of Neumann and Curie are of course based on classical physics. They remain valid for quantum systems but do not include typical quantum phenomena, such as the existence of electronic degeneracy or transitions between quantum states. A proper quantum description of molecular symmetry is thus required.

5.2 The Schrödinger Equation

According to quantum mechanics, the stationary states of a molecule are described by the eigenfunctions of the Hamiltonian, $\mathcal{H}$, corresponding to a quantized set of eigenvalues,

$$\mathcal{H}|\Psi_j^k\rangle = E_k|\Psi_j^k\rangle \tag{5.3}$$

Here, E_k is a fixed eigenvalue, and $|\Psi_j^k\rangle$ is an associated eigenfunction. The index j takes into account the possibility that several eigenfunctions may be associated with the same eigenvalue. In this case the set of these functions forms an eigenspace $\{|\Psi_j^k\rangle\}_{j=1,\ldots,n}$, where n denotes the dimension of this space, and the E_k eigenvalue is said to be n-fold *degenerate*. As usual, the eigenspace will be taken to be orthonormal. The Hamiltonian expresses the kinematics of the electrons in the frame of the nuclei subject to Coulomb forces. We shall study this in detail in Sect. 5.4. For the moment, all we need to know is that the operators of the molecular point group leave $\mathcal{H}$ invariant:

$$\forall\ \hat{R} \in G \rightarrow [\hat{R}, \mathcal{H}] = 0 \tag{5.4}$$

Now applying $\hat{R}$ to the Schrödinger equation yields

$$\hat{R}\mathcal{H}\left|\Psi_j^k\right\rangle = \mathcal{H}\hat{R}\left|\Psi_j^k\right\rangle = E_k\hat{R}\left|\Psi_j^k\right\rangle \tag{5.5}$$

Here, we have made use of the commutation relation in Eq. (5.4) and the property that $\hat{R}$ as a linear operator does not affect the constant eigenvalue. The equation signifies that if $|\Psi_j^k\rangle$ is an eigenfunction, the transformed function, $\hat{R}|\Psi_j^k\rangle$, also is an eigenfunction *with the same eigenvalue*. This is an important result, which ties quantum mechanics and group theory together, and is essentially the reason why group theory can be applied to chemistry! Now, there are two possibilities, depending on the degeneracy.

1. The electronic state is nondegenerate ($n = 1$). In this case the transformed eigenfunction must necessarily be proportional to the original one. Since the transformation does not change normalization, the proportionality constant must be a

unimodular number:

$$\hat{R}\left|\Psi^k\right\rangle = \exp(i\kappa_R)\left|\Psi^k\right\rangle \tag{5.6}$$

Here, we have dropped the index j since there is only one eigenfunction in this case. This equation indicates that this eigenfunction must transform as a nondegenerate irrep of the point group, say Γ_k, with

$$\exp(i\kappa_R) = \chi^{\Gamma_k}(R) \tag{5.7}$$

2. The electronic state is degenerate ($n > 1$). In this case the transformed function may not be proportional to the original one, but in any case it is also an eigenfunction of H with the same eigenvalue. This means that it must be mapped onto a linear combination of the components of the eigenspace; hence, the eigenspace itself must form a function space that is invariant under G:

$$R\left|\Psi_j^k\right\rangle = \sum_{i=1}^{n} D_{ij}(R)\left|\Psi_i^k\right\rangle \tag{5.8}$$

Here, the eigenfunctions have again been arranged as a row vector, and the coefficients are gathered in a transformation matrix, $\mathbb{D}(R)$. There are now two possibilities:

- The matrix representation is an irrep of the point group.
  In this case the electronic degeneracy is equal to the dimension of an irrep of the point group.
- The matrix representation is reducible.
  In this case the eigenspace can always be separated in irreducible blocks by using projection operators.

This list of possibilities shows that eigenfunctions of the Hamiltonian will also be (or can be made to be) eigenfunctions of the symmetry group of the Hamiltonian. When there is a perfect match between the eigenfunctions and an irrep, the presence of degeneracy or nondegeneracy can directly be attributed to the symmetry of the eigenstates. The remaining possibility that the eigenspace may consist of several irreducible blocks could be described as a case of "accidental degeneracy", in the sense that symmetry cannot explain the fact that stationary states are degenerate. When this happens, it could mean that the symmetry of the system exceeds the apparent spatial symmetry group. This case is referred to as "hidden symmetry". A special case of this is Kramers' degeneracy, which is treated in Sect. 7.6. Or it could be that a simplified model Hamiltonian was used, such as, e.g., the nearest-neighbor Hamiltonian in Hückel theory, which may give rise to additional degeneracies, as we have explained for the example of triphenylmethyl in the previous chapter. In addition to these possibilities—in the words of Griffith [2]—experience tells that "accidents don't happen, at least in that part of physics which is understood".

The significance of these observations can hardly be overestimated. The derivation refers to the properties of the exact Hamiltonian and its eigenfunctions. In actual

calculations one must usually introduce approximate Hamiltonians and eigenspaces. However, there is at least one simple way to endow these approximate eigenfunctions with an exact property, i.e., by making sure that they are eigenfunctions of the symmetry group of the exact Hamiltonian. The great success of semiempirical theories, such as ligand-field theory for transition-metal and lanthanide complexes, is in fact due to this consistent use of atomic and molecular symmetry. But also in computational chemistry the effort of symmetrizing the orbital basis pays off in a considerable gain of computation time, and it facilitates the assignment of spectroscopic data.

5.3 How to Structure a Degenerate Space

The eigenfunctions of an n-fold degenerate state are defined up to unitary equivalence, which means that any complex linear combination of eigenfunctions is again an eigenfunction. It is convenient to define a standard basis, which brings some structure in this degenerate space. The tool that can be used for this is furnished by the following lemma due to Schur.

Theorem 11 *If a matrix commutes with all the matrices of an irreducible representation, the matrix must be a multiple of the unit matrix*:

$$\forall\ \hat{R} \in G : \mathbb{U}\mathbb{D}(R) = \mathbb{D}(R)\mathbb{U} \rightarrow \mathbb{U} \sim \mathbb{I} \tag{5.9}$$

This theorem implies that, if we combine the basis functions of a space in such a way that their representation matrices of the group generators coincide with a canonical choice, then the entire basis set will be completely fixed, up to a global phase factor. This remaining phase freedom is external to the symmetry group. A basis set that complies with a specified set of representation matrices is called a *canonical* basis. A convenient strategy for defining a canonical basis is founded on a *splitting field*. In this case the basis is chosen in such a way that it is diagonal with respect to a particular generator, usually a principal axis of rotation. The components then appear as eigenfunctions of the splitting field. In order for the splitting to be unequivocal, all eigenvalues should be different. The splitting field then "recognizes" each component by its individual eigenvalue. As an example, consider the twofold degenerate E-state in an octahedron. As a splitting field, we take the $\hat{C}_4$ axis along the z-direction. The standard components, which are recognized individually by this field, are denoted as $|E\theta\rangle$ and $|E\epsilon\rangle$. They are respectively symmetric and anti-symmetric with respect to the rotation axis:

$$\begin{aligned} \hat{C}_4^z|E\theta\rangle &= |E\theta\rangle \\ \hat{C}_4^z|E\epsilon\rangle &= -|E\epsilon\rangle \end{aligned} \tag{5.10}$$

In octahedral transition-metal complexes, the d-orbitals, which transform as the E irrep, are d_{z^2} and $d_{x^2-y^2}$. They are seen to match $|E\theta\rangle$ and $|E\epsilon\rangle$, respectively. The

conventional choice of the real d-orbitals is thus based on a tetragonal splitting field. Once the splitting field has been applied, the eigenspace is already nearly fixed; the only freedom that remains is the *relative* phases of the components. To freeze these phases, one can sometimes use an extra ladder operator, which moves from one component to the other, thereby imposing a phase convention. For the E-state, one uses a threefold axis to connect the two components, and the corresponding representation matrix is defined by

$$\hat{C}_3\left(|E\theta\rangle \quad |E\epsilon\rangle\right) = \left(|E\theta\rangle \quad |E\epsilon\rangle\right)\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \tag{5.11}$$

This operator connects the two components, and, therefore, if we require that the matrix be of the specified form, then the relative phase freedom is lifted. With such a connecting element, one can indeed easily construct a proper ladder operator:

$$\begin{aligned} \frac{2}{\sqrt{3}}\left[\hat{C}_3 + \frac{1}{2}\hat{E}\right]|\hat{E}\theta\rangle &= |\hat{E}\epsilon\rangle \\ -\frac{2}{\sqrt{3}}\left[\hat{C}_3 + \frac{1}{2}\hat{E}\right]|\hat{E}\epsilon\rangle &= |\hat{E}\theta\rangle \end{aligned} \tag{5.12}$$

In Appendix D we list standard conventions that are frequently used to define canonical basis sets for degenerate irreps.

For the octahedral T_1 state, the standard basis complies with the transformation properties of the real p-orbitals and is marked as $|T_{1x}\rangle, |T_{1y}\rangle, |T_{1z}\rangle$. If we diagonalize this set under a fourfold splitting field, we obtain the complex p-orbitals. In applications where real functions are preferred, the $\hat{C}_4$ axis is represented as

$$\hat{C}_4\left(|T_{1x}\rangle \quad |T_{1y}\rangle \quad |T_{1z}\rangle\right) = \left(|T_{1x}\rangle \quad |T_{1y}\rangle \quad |T_{1z}\rangle\right)\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{5.13}$$

Here, $|T_{1z}\rangle$ is recognized as a totally symmetric eigenfunction, and it is uniquely defined by this eigenvalue since the other eigenvalues are $\pm i$. The splitting field is thus operating only partially; nonetheless, it uniquely picks the z-component. Then the $\hat{C}_3$ axis is a perfect ladder operator, effecting a cyclic permutation of z to x, and further to y.

5.4 The Molecular Symmetry Group

So far, the symmetry of the Hamiltonian was defined as the set of all operations that leave the Hamiltonian invariant. This invariance group was assumed to coincide with the point group of the nuclear frame of the molecule, but it is now time to provide a clear explanation of this connection. This section relies on the definition of the

symmetry groups of nonrigid molecules proposed by Longuet-Higgins [3]. We start by writing down in explicit form the Schrödinger Hamiltonian for a molecule:

$$\mathcal{H} = T_e + T_N + V_{NN} + V_{eN} + V_{ee} \tag{5.14}$$

The T operators are the kinetic energy operators for electrons and nuclei:

$$\begin{aligned} T_e &= -\frac{\hbar^2}{2m_e}\sum_i\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right) \\ T_N &= -\frac{\hbar^2}{2}\sum_n\frac{1}{m_n}\left(\frac{\partial^2}{\partial X_n^2}+\frac{\partial^2}{\partial Y_n^2}+\frac{\partial^2}{\partial Z_n^2}\right) \end{aligned} \tag{5.15}$$

The V operators are the Coulomb interactions between the particles:

$$\begin{aligned} V_{NN} &= \sum_{n<m}\frac{Z_n Z_m \mathrm{e}^2}{4\pi\epsilon_0|\mathbf{R}_n-\mathbf{R}_m|} \\ V_{eN} &= -\sum_{i,n}\frac{Z_n \mathrm{e}^2}{4\pi\epsilon_0|\mathbf{R}_n-\mathbf{r}_i|} \\ V_{ee} &= \sum_{i<j}\frac{\mathrm{e}^2}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|} \end{aligned} \tag{5.16}$$

The Hamiltonian may contain additional terms describing coupling between orbital and spin momenta. Longuet-Higgins stated that this full Hamiltonian must be invariant under the following types of transformations:

1. Any permutation of the positions and spins of the electrons.
2. Any rotation of the positions and spins of all particles (electrons and nuclei) about any axis through the center of mass.
3. Any over-all translation in space.
4. The reversal of all particle momenta and spins.
5. The simultaneous inversion of the positions of all particles in the center of mass.
6. Any permutation of the positions and spins of any set of identical nuclei.

The complete group of the Hamiltonian is the combination of all these possible symmetries. This derivation is directly evident from the mathematical form of the Hamiltonian and expresses fundamental properties of molecular space and time. Yet it took 40 years, from Schrödinger to Longuet-Higgins, to obtain a clear definition of the molecular-symmetry group. Three kinds of symmetries may be identified:

- Space symmetries. Space is uniform, isotropic, and has inversion symmetry. This is clear from the fact that the kinetic energy Laplacian operators are trace operators of second derivatives; hence, they are invariant under a sign change of all coordinates and isotropic under rotations. All potential-energy operators depend only on relative distances between particles and thus do not change under translations, rotations, or inversion.

- Time symmetry. The reversal of all momenta and spins is nothing other than the time-reversal operator we introduced earlier. As long as no external magnetic fields are present, time is reversible.
- Elementary particles of the same kind are indistinguishable. The remaining symmetries do not refer to space or time but to the permutational symmetry of a set of particles. All electrons are the same, and thus the Hamiltonian does not change when we permute electron labels. This symmetry becomes apparent only when multielectronic wavefunctions are considered, and these will be treated in the next chapter. Likewise, identical nuclei can be permuted without changing the Hamiltonian. This is reflected in the potential energy terms, which consist of sums over all pairwise interactions. Permutations of particle labels change only the order of the terms in these summations.

As an example, in Fig. 5.1 we return to our favored ammonia molecule and list all nuclear permutations, with and without the all-particle inversion operator, that leave the full Hamiltonian invariant. Nuclear permutations are defined here in the same way as in Sect. 3.3. A permutation such as (ABC) means that the letters A, B, and C are replaced by B, C, and A, respectively.[1] The inversion operator, $\hat{E}^*$, inverts the positions of all particles through a common inversion center, which can be conveniently chosen in the mass origin. In total, 12 combinations of such operations are found, which together form a group that is isomorphic to D_{3h}. How is this related to our previous C_{3v} point group? At this point it is very important to recall that the state of a molecule is not only determined by its Hamiltonian but also, and to an equal extent, by the boundary conditions. The eigenvalue equation is a differential equation that has a very extensive set of mathematical solutions, but not all these solutions are also acceptable states of the physical system. The role of the boundary conditions is to define constraints that filter out physically unacceptable states of the system. In most cases these constraints also lead to the quantization of the energies.

From our present perspective the invariance group should not only leave the Hamiltonian invariant, but also *it should not alter the boundary conditions*. Now, in most quantum-chemical applications a very stringent boundary condition is offered by the Born−Oppenheimer approximation. This simply states that the nuclei are considered immobile. It seriously restricts the Longuet-Higgins list. Indeed, we should retain only those operations that leave all nuclei in their rest positions. Applying this to ammonia, of the twelve operations we retain only those that do not affect the starting structure, i.e., only those combinations of permutations, permutation inversion, and overall rotations that, as a net result, keep the nuclei fixed in space. This immediately constrains the symmetry group to the familiar C_{3v} molecular point group. As an example, the permutation of nuclei B and C followed by the inversion of all particles gives rise to the structure, marked (A)(BC)* in Fig. 5.1, in which the ammonia molecule has been turned upside down. The nuclei can be moved back to their original positions by rotating the whole molecule by 180° about

[1] See also [4, Chap. 1].

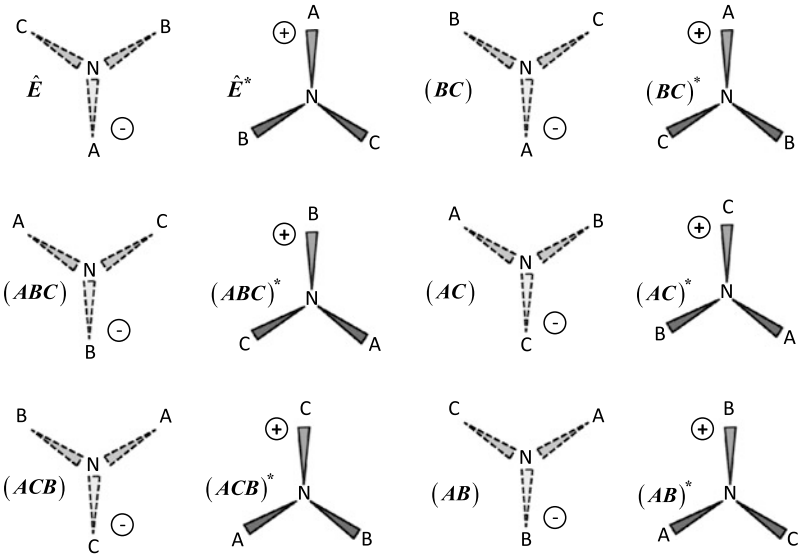

Fig. 5.1 Dynamic symmetry group of ammonia, with permutations of nuclei, and inversion of all particles (indicated by *an asterisk*). *The plus* (*minus*) *sign* indicates the position of an electron above (below) the plane of the hydrogen atoms

Table 5.1 Embedding of the C_{3v} point group in the Longuet-Higgins group. The symmetry elements of the point group act on the electrons. They are identified as the product of nuclear permutations, inversion of all particles (star operation), and bodily rotations of all particles ($\hat{\mathcal{Q}}$ operators) along particular directions

C_{3v}	Rotation	×	Inversion	×	Permutation
$\hat{E}$	$\hat{E}$		$\hat{E}$		$\hat{E}$
$\hat{C}_3$	$\hat{\mathcal{Q}}_3^z$		$\hat{E}$		(ABC)
$\hat{C}_3^2$	$(\hat{\mathcal{Q}}_3^z)^{-1}$		$\hat{E}$		(ACB)
$\hat{\sigma}_1$	$\hat{\mathcal{Q}}_2^{\perp\sigma_1}$		$\hat{E}^*$		(A)(BC)
$\hat{\sigma}_2$	$\hat{\mathcal{Q}}_2^{\perp\sigma_2}$		$\hat{E}^*$		(B)(AC)
$\hat{\sigma}_3$	$\hat{\mathcal{Q}}_2^{\perp\sigma_3}$		$\hat{E}^*$		(C)(AB)

an axis that is perpendicular to the $\hat{\sigma}_1$ reflection plane. The net result is that the electron, marked by the little circle in the figure, has been reflected in this plane. This operation thus leaves the nuclei in place, and only the positions of the electrons are changed. This is precisely the definition of symmetry operators that we have been using all along. The operators are displacing the electrons and in this way lead to transformations of the electronic wavefunctions. The complete embedding of C_{3v} in the Longuet-Higgins group is given in Table 5.1.

By contrast, an operation such as (A)(BC), not followed by spatial inversion of all particles, gives rise to an alternative arrangement of the nuclei, which cannot be brought into coincidence with the original positions by mere spatial rotations. As a result, this operation is not compatible with the Born−Oppenheimer boundary con-

ditions. On the other hand, going beyond the Born−Oppenheimer approximation, one may consider the dynamic states of ammonia that correspond to the tunnelling of the nitrogen through the triangle of the hydrogens. For the tunnelling states, the all-particle inversion operator, $\hat{E}^*$, is also a symmetry element, and the symmetry group of the nonrigid ammonia thus attains the full D_{3h} Longuet-Higgins group.

5.5 Problems

5.1 Prove that the electron-repulsion operator, V_{ee}, is invariant under the rotation around the z-axis.

5.2 Construct a splitting field and ladder operators for the canonical components of the icosahedral irreps in Appendix D.

5.3 Derive the permutation–inversion group for CH_3BF_2 (methyl-boron-difluoride) under the assumption that the methylgroup is almost freely rotating. This means that the result of a permutation inversion can be rotated back by a bodily rotation to a rotamer of the original structure. Determine the point group that is isomorphic to the resulting dynamic symmetry group.

5.4 The barrier to rotation of the cylopentadienyl rings in $Fe(C_5H_5)_2$ (ferrocene, see Fig. 3.9(a)), measured in the gas phase, is only a kcal/mol. Construct a dynamic symmetry group for this molecule.

References

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