

6 Applications of (mostly) finite groups

6.3 Electron orbit of an atom

A very similar line of argument can be applied to constrain quantum dynamics using symmetry.

Suppose that we want to study how electrons move in an atom, which must be formulated using quantum mechanics. The fundamental equation of motion to use now is Schrödinger's equation, instead of Newton's law.

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = H\Psi(\vec{r}, t) \quad (1)$$

We look for states with a periodic time dependence of the form $\Psi(\vec{r}, t) = \Psi_0(\vec{r})e^{-i\omega t}$ and the equation reduces to

$$H\Psi_0(\vec{r}) = \hbar\omega\Psi_0(\vec{r}) \quad (2)$$

which is the eigenvalue equation for H . In the Hilbert space of the electron, H is a Hermitian operator and has a complete set of orthogonal eigenstates with real eigenvalue (which corresponds to the energy of the eigenstates). Note that the Hilbert space of the electron is infinite dimensional.

If the system has certain symmetry which is represented on the Hilbert space as $D(g)$, then

$$D^{-1}(g)HD(g) = H \quad (3)$$

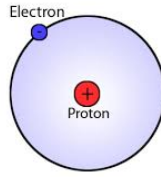
Now the algebra becomes exactly the same as in the classical case, and we can reach the same conclusion:

(1) The degenerate subspaces of eigenstates of H transform as irreps. Eigenstates in the same irrep must be degenerate (have the same energy) while states in different irreps (which may or may not be equivalent to each other) generically have different energy.

(2) Once we have figured out all the irreps contained in $D(g)$, the eigenstates are obtained through linear combinations of equivalent irreps. Inequivalent irreps cannot be superposed to form eigenstates.

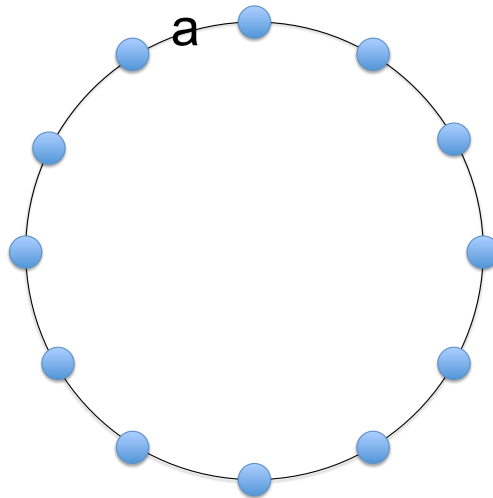
Example: consider the electron orbit in a Hydrogen atom. The system (the Hamiltonian of the electron) is invariant under rotation around the z axis (pointing out of plane), which forms a circle group symmetry. Therefore, the eigenstates (orbitals) of the electron can be labeled by an integer, which labels different irreps of the circle group. Corresponding to the same integer, hence the same irrep of the circle group, there may be different eigenstates of different eigen energies. Irreps labeled by different integers cannot be mixed to form eigenstates.

This integer is directly proportional to the z direction angular momentum of the electron orbital. In fact, the Hydrogen atom has full three dimensional rotation symmetry, not just rotation symmetry around z axis. We are going to explore its consequence after we have learned more about continuous groups.



6.4 Electron wave function on a lattice

Let's consider the example of an electron moving in a one dimensional chain with discrete translation symmetry. Instead of thinking about infinite system at the beginning, let's start from a finite size lattice and later take the limit of system size going to infinity. To preserve translation symmetry in a finite system, we use the so-called '**periodic boundary condition**' and put the system on a ring.



Suppose that the system contains N regularly spaced atoms and the electron moves in their potential. The hamiltonian

$$H = \frac{p^2}{2m} + V(x) \quad (4)$$

is invariant under translation by lattice constant a , generated by $e^{ipa/\hbar}$. The fact that $e^{ipa/\hbar}$ generates translation can be seen from

$$e^{ipa/\hbar} x e^{-ipa/\hbar} = x + a \quad (5)$$

which can be deduced from the commutation relation between p and x , $[x, p] = i\hbar$.

Translation symmetry then forms a C_N group. The hamiltonian of the electron being translation invariant means that each of the eigenstates corresponds to one of the irreps of C_N . C_N has N irreps, given by

$$1, \omega, \omega^2, \omega^3, \dots, \omega^{N-1}, \omega = e^{i2\pi n/N}, n = 0, 1, \dots, N-1 \quad (6)$$

Each irrep is labeled by n , which is an integer mod N .

Define quantity

$$k \equiv \frac{2\pi n}{Na} \quad (7)$$

where a is the lattice constant (physical distance between two lattice sites). k is called the wave number of the wave function. $\hbar k$ is called the **crystal momentum** of the electron. The irrep labeled by n can then be labeled by k and the representation matrices (numbers) are give by

$$1, \omega, \omega^2, \omega^3, \dots, \omega^{N-1}, \omega = e^{ika}, \quad k = 0, \frac{2\pi}{Na}, \frac{4\pi}{Na}, \dots, \frac{2\pi(N-1)}{Na} \quad (8)$$

Now imagine taking the limit of N going to infinity. The possible values of k increase in number, and eventually populate every point between 0 and $\frac{2\pi}{a}$. Equivalently, we can take k to take value between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$ because of the periodicity of k .

Recall the result we obtained previously.

The (degenerate subspaces of) eigenstates of a Hamiltonian transform as irreps of the symmetry group of the Hamiltonian.

Which means

The eigenstates transform under the symmetry, and the transformation matrix is exactly given by the representation matrix in the corresponding irrep.

Let's see how this conclusion applies to our case of lattice translation symmetry.

A consequence of translation symmetry is that, every eigenstate of the electron corresponds to an irrep of the translation symmetry labeled by k . That is, the wave function $\Psi(r)$ transforms under translation as

$$T(a)\Psi(r) = e^{ika}\Psi(r) \quad (9)$$

It can be shown that the wave function takes the form

$$\Psi(r) = e^{ikr}u(r) \quad (10)$$

where r labels positions on the ring and $u(r)$ is a periodic function with period a . That is $u(r)$ is invariant under translation along the lattice. Let's check how the total wavefunction transforms under translation symmetry

$$T(a)\Psi(r) = \Psi(r+a) = e^{ik(r+a)}u(r+a) = e^{ika}e^{ikr}u(r+a) = e^{ika}\Psi(r) \quad (11)$$

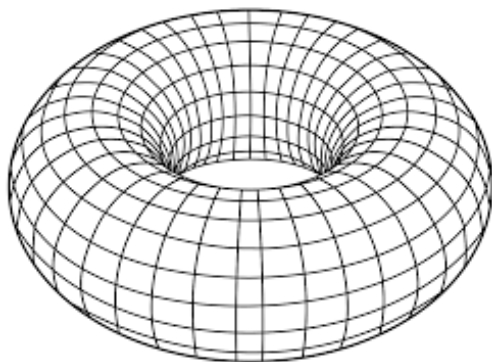
That is, $\Psi(r)$ indeed forms a 1D rep of the translation symmetry labeled by k , as we would have expected.

Now let's move on to two dimension and consider first the square lattice. Imagine a square lattice on the surface of a torus with periodic boundary conditions in both directions. We have translation symmetry in both x and y direction and it forms a $C_{N_x} \times C_{N_y}$ group. The irreps of the $C_{N_x} \times C_{N_y}$ group is labeled by two integers n_x and n_y and following previous argument we can see that the wave function of each eigenstate takes the form

$$\Psi(\vec{r}) = e^{i(k_x r_x + k_y r_y)}u(\vec{r}) = e^{i\vec{k} \cdot \vec{r}}u(\vec{r}) \quad (12)$$

where $u(\vec{r})$ is invariant under translation in both directions and $k_x = \frac{2\pi n_x}{N_x a_x}$, $k_y = \frac{2\pi n_y}{N_y a_y}$ gives the crystal momentum of the electron in x and y directions (when multiplied with \hbar).

This result can be generalized to other lattices in 2D and 3D and is summarized by **Bloch's theorem**:



The energy eigenstates for an electron in a crystal takes the form

$$\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) \quad (13)$$

where $u(\vec{r})$ is a periodic function with the same period as the lattice, $\hbar\vec{k}$ is the crystal momentum of the electron and \vec{k} takes value in a so-called '**Brillouin zone**'. In 1D, the Brillouin zone is $[-\frac{\pi}{a}, \frac{\pi}{a}]$. In 2D with square lattice, the Brillouin zone is a rectangle region between $[-\frac{\pi}{a_x}, \frac{\pi}{a_x}]$ in the k_x direction and $[-\frac{\pi}{a_y}, \frac{\pi}{a_y}]$ in the k_y direction. For more complicated lattices, the Brillouin zone takes more complicated shapes.

$\Psi(\vec{r})$ of this form is called a Bloch wave.

Each eigenstate will have a corresponding energy given by the Hamiltonian. Imagine that we move along the k axis in the 1D Brillouin zone. As k is densely populated in the Brillouin zone, we expect the energy to change with k in a smooth way. If we plot energy versus k , we get a smooth line, forming a so called **energy band**. Moreover, there can be multiple states with the same k but different energy. That means we can have multiple bands in the crystal. If we plot them all out, we get the **band structure** of the crystal. This can be done for 2D and 3D lattice as well, although it is harder to draw. The band structure is the most important notion in solid state physics.

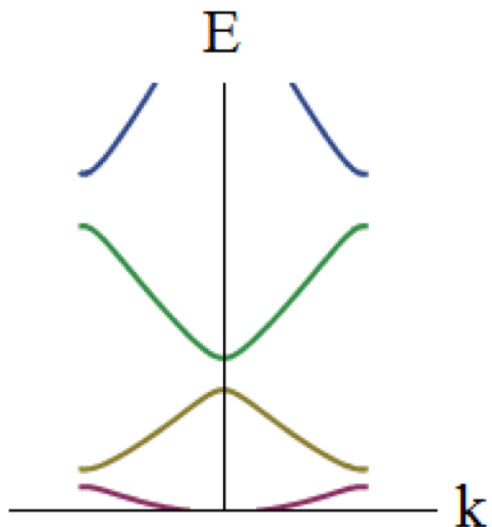


Figure 1: An example of a 1D band structure.