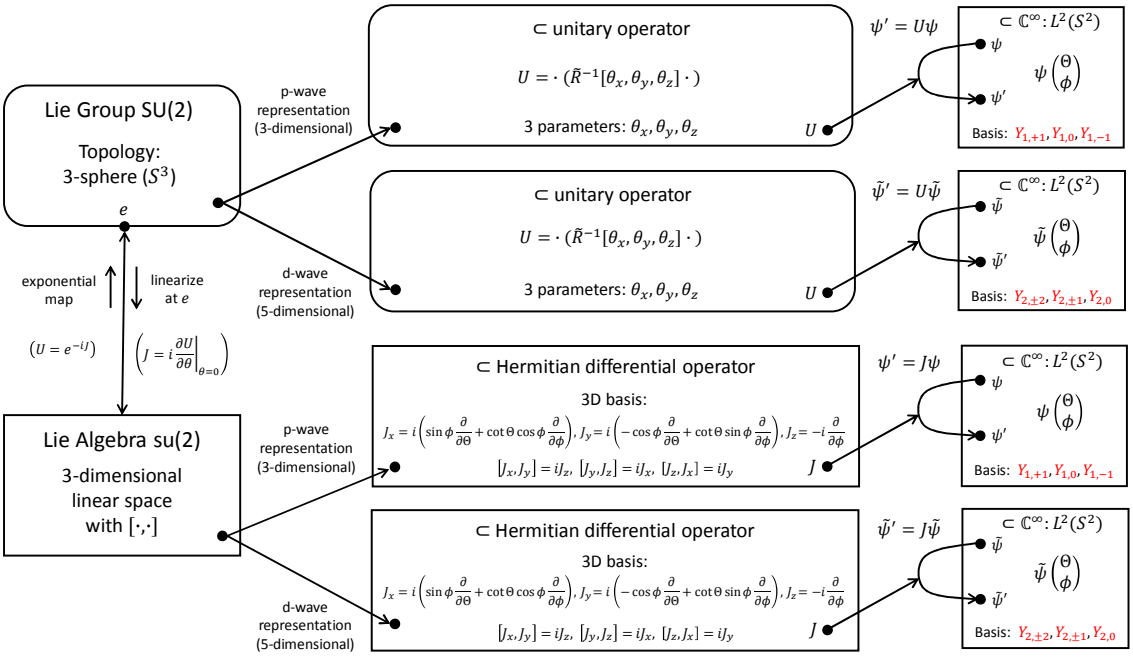
3.13 SU(2): Application to Electron Orbitals; Reducible Representations



We continue to explore the infinite-dimensional representation of SU(2) from the previous example, but from now on we'll ignore the radial direction of the representation space and focus on just the unit sphere where our functions can be written as $\psi(\Theta, \phi)$.

Unlike the finite-dimensional representations that we discussed earlier, this infinite-dimensional representation is *reducible*, that is, it can be broken up into sub-representations. In other words, the infinite-dimensional representation space can be divided up into subspaces that get mapped to themselves. Thus, each subspace furnishes a valid representation of SU(2)! How can we identify these subspaces? Remember that the eigenvalues of the Casimir operator J_C^2 can be used to delineate irreducible representations? We already know that the eigenvalues of J_C^2 are $j(j+1)$ and thus j directly labels these subspaces! Subspace j consists of the (complex) linear combinations of the basis functions $Y_{j,m}(\Theta, \phi)$ with $m = 0, \pm1, \pm2, \ldots \pm j$. Since there are $2j+1$ such basis functions the irreducible sub-representations are $(2j+1)$-dimensional. The diagram shows two such sub-representations, one for $j = 1$ with three basis functions (upper branch) and one for $j = 2$ with five basis functions (lower branch). When applied to electron orbitals in atoms, the electron wave functions furnishing the 3-dimensional representation are known as *p-waves* and those furnishing the 5-dimensional representation as *d-waves*.

We can pick any function within an invariant subspace (= a complex linear combination of the respective basis functions), rotate it arbitrarily in 3D space, and get again a function in that same space. For example for the subspace $j = 1$, we can pick the dumbbell-shaped basis function $Y_{1,0}(\Theta, \phi)$, rotate the z axis into the x axis, and then express the result as a combination of the remaining two basis functions $\frac{1}{\sqrt{2}}[Y_{1,-1}(\Theta, \phi) - Y_{1,+1}(\Theta, \phi)]$. Similarly, if we rotate the z axis into the y axis, we can express the result as $\frac{1}{\sqrt{2}}i[Y_{1,-1}(\Theta, \phi) + Y_{1,+1}(\Theta, \phi)]$. (See [FLP, Vol. III, Ch. 19-5] for more details.)

Why does the space of wave functions in quantum mechanics have invariant subspaces? Subspace j contains all possible wave functions with the (definite) total angular momentum j. Rotating such a wave function arbitrarily in 3D space does *not* change its total angular momentum, it only changes the angular momentum's orientation in space (or, equivalently, its z component). Thus, the rotated wave function must again be a member of the subspace j.

At first glance, the subspaces may appear to be infinite dimensional because they contain functions that take on values at infinitely many (Θ, ϕ) points. However, this is an illusion because all functions in a given subspace can be constructed from just the $2j+1$ basis function and thus are fully specified by $2j+1$ (complex) coefficients. In fact, we can "unpack" the functions belonging to a subspace and write them as $(2j+1)$-dimensional vectors. This is analogous to how we unpacked the matrices in the adjoint representation into simple vectors. When we unpack the functions into $(2j+1)$-dimensional vectors, we also have to unpack the transformations in the Lie group and the differential operators in the Lie algebra (the generators) into $(2j+1)\times(2j+1)$ matrices.

For example, a general function in our 3-dimensional subspace can be written as $\psi = z_1 Y_{1,+1} + z_2 Y_{1,0} + z_3 Y_{1,-1}$ or, more explicitly, as $\psi = -z_1 \frac{1}{\sqrt{2}} \sin\Theta\, e^{i\phi} + z_2 \cos\Theta + z_3 \frac{1}{\sqrt{2}} \sin\Theta\, e^{-i\phi}$ and is fully specified by the complex vector $(z_1, z_2, z_3)^T$. Now, if we act with the differential operator $J_z = -i\partial/\partial\phi$ on this function, we get $\psi' = -z_1 \frac{1}{\sqrt{2}} \sin\Theta\, e^{i\phi} - z_3 \frac{1}{\sqrt{2}} \sin\Theta\, e^{-i\phi}$. Comparing this to the general subspace function $\psi' = -z_1' \frac{1}{\sqrt{2}} \sin\Theta\, e^{i\phi} + z_2' \cos\Theta + z_3' \frac{1}{\sqrt{2}} \sin\Theta\, e^{-i\phi}$, we find that $z_1' = z_1$, $z_2' = 0$, and $z_3' = -z_3$. Thus, the unpacked generator is just the familiar 3×3 matrix for rotating spin-1 particles about the z axis! Repeating this procedure for the remaining two generators, J_x and J_y, confirms that the *p*-wave representation is isomorphic to the 3-dimensional representation on vectors we discussed earlier. Similarly, the *d*-wave representation is isomorphic to the 5-dimensional representation on vectors.

We have thus discovered a method for constructing new irreducible representations from old ones: From a known finite-dimensional representation construct an infinite-dimensional representation on functions. Then, with the help of the Casimir operator, break this infinite-dimensional representation into finite-dimensional irreducible representations. It is possible to obtain *all* irreducible representations of SU(2) in this way (not just the odd-dimensional ones, as suggested by our example) [QTGR, Ch. 8.2].

We are now in a position to understand an important aspect of the *electron orbitals* in atoms. Compact and stationary electron wave functions have discrete and definite energy levels. But not every basis wave function of the electron in the *rotationally symmetric* atom has its *distinct* energy level! Rotational symmetry dictates that wave functions that belong to the same irreducible representation of SU(2) have the *same* energy (as well as the same total angular momentum). For a given total angular momentum *j* there are $2j+1$ basis wave functions with the same energy (but different orientations in space). In atoms, the lowest energy level belongs to the spherical *1s* orbital; the next one up is the spherical *2s* orbital followed by three dumbbell-shaped *2p* orbitals with the *same* energy but three different orientations; then there is one *3s*, followed by three *3p*, followed by five *3d* orbitals, etc. Here the number indicates the electron *shell* and the letter the *subshell* to which the orbital belongs. All orbitals within the same subshell have the same energy. This $(2j+1)$-fold degeneracy has important consequences for how the electrons fill up the shells, which, in turn, determines the structure of the periodic table of the elements. (See [FLP, Vol. III, Ch. 19-6] for more details.)