1. Hello and welcome to this short animated pencast on molecular group theory. (4.3s)
2. Today we will discuss benzene. (2.5s)
3. More specifically, we will discuss the symmetry of the basis set consisting of the collection benzene’s individual pz orbitals. (6s)
4. In fact, to make the orbitals easier to see, I will make the atoms smaller.
5. Benzene belongs to the D6h point group, which means we will make use of the D6h point group character table to find out which symmetry operations can be applied to benzene. (9s)
6. Our first task will be to understand and analyze the effect of each symmetry operation on our basis set. We will store this information in the form of a vector, referred to as the reducible representation of our basis set. (5s)

As is often the case with vectors, and as indicated by its name, the reducible representation can be expressed as a collection, or for the more mathematically inclined among you, as a linear combination of its linearly independent constituents, commonly called irreps. Our second and final task in this pencast, will be to use the little orthogonality theorem to find out which irreps from the character table make up our reducible representation. (11s)

1. But first, some rules. (2s)

When constructing the reducible representation, we apply each symmetry operation to the entire benzene molecule. We then observe what happens to the position and orientation of each pz orbital to determine its contribution.

1. The first case we will be looking at is the one in which an orbital stays in place with unchanged orientation. That orbital is said to have a trace of one, which is its contribution to the reducible representation under that transformation. Orbitals that stay in place will be highlighted with a glowing animation. (14s)
2. The second case is when a symmetry operation does not change the position, but inverts the orientation of an orbital, in this case, this orbital is attributed a trace of -1 under this operation. Orbitals which stay in place with inverted orientation will also be highlighted also be with a glowing animation. (9s)
3. Finally, for the third case, if the orbital leaves its starting position during the symmetry operation, a trace of zero is attributed to it, as the orbital is not symmetrical under this symmetry operation. For contrast with the case in which orbitals do stay in place, those that leave their starting position during an operation will become transparent(9s).
4. With this, we can start analyzing each of the symmetry operations applicable to the D6h point group. Storing the trace of each operation in the bottom left corner of the screen for clarity. (8s)
5. We start with the identity operation, which is associated with the action of doing no action. In which case, all orbitals stay in place with unchanged orientation. Therefore, the trace associated with each orbital is 1, adding up to a total of 6(9s).
6. Next we have 2 C\_6 rotations along the z axis, which is perpendicular to the molecular plane. In this case, all orbitals leave their starting position giving each one an associated trace of 0. Making up for a total of 0.
7. Note how the trace of both C6 rotations is the same. This is no coincidence. If two symmetry operations have the same label, like the clock-wise and counter-clockwise rotations under the C6 label. They will necessarily have the same effect on our basis set. What this means is that for operations like the C6 rotation, we only need to consider one of the transformations, then multiply the associated trace by the number of operations under the same label.
8. Following this logic, we only need to consider one of the C3 rotations along the z axis. Which has a trace of 0. There are two C3 rotations, giving this operation a trace of 2 times 0, which still equals zero.
9. Next we have a C2 rotation along the z axis. Just as the last two rotations, this one also has a trace of 0.
10. Now we have the C2’ rotations. Each rotation leaves two atoms in place, but inverts their orientation. Giving each rotation a trace of minus 2, making up for a total of -6 when all rotations are considered.
11. Now we have the C2’’ rotation. This rotation happens about carbon-carbon bonds, hence all orbitals leave their starting position. Giving this operation a trace of 0;
12. Next, we have the horizontal mirror plane of reflection. Since the refection happens across eachcarbon atom, none of them leave their starting positions. Furthermore, since the pz orbitals are orthogonal to this mirror of reflection, all have their orientation inverted. Giving this operation a trace of -6.
13. Next we have the inversion operation. Since all carbon atoms leave their starting positions. This operation has a trace of 0.
14. Next we have the reflections about the vertical mirror planes. Since each plane crosses two carbon atoms, each keeps two orbitals in place. Since there are a total of 3 mirrors of reflection and the orientation of the orientation of the orbitals does not change, this operation has a trace of 6.
15. Next we have reflection about the dihedral mirror planes. Since this operation happens about the bonding axes, just as with the C’’ rotations, all carbon atoms leave their starting positions. Attributing their respective pz orbitals a value of zero. Giving this operation a trace of 0;
16. With this we have seen all symmetry operations of benzene applied to the basis set consisting of its pz orbitals. Now we can construct the overall trace for this basis set and express it in terms of its constituent irreps (11s).
17. To do this, we count how many times each irrep appears in the trace. This can be done with the little orthogonality theorem. That is, by taking the dot product between each irrep with the trace and dividing by the product of the length of both vectors, as can be seen with the A1g irrep. (14s)
18. This operation gives 0, but that is not the case for all irreps. In any case, the application of the little orthogonality theorem for all irreps can be found here. Feel free to pause and check all of them by yourself (11s):
19. Carrying on this computation to all irreps reveals that our trace can be decomposed into the following linear combination of irreps (you can check this by adding them up) (10s):

Show the linear combination

With this we have reached our objective of finding the irreducible representations that fully describe the symmetry of the basis set made up by the pz orbitals in the carbon atoms of the benzene molecule.

But we are not done just yet. Though I won’t go into the details in this video, I think it is very interesting to note that once the irreps are known, further processing can be done to find out which linear combinations of atomic orbitals would have the symmetries described by each irrep. These of course, can be plotted to show the possible symmetries hidden in the basis set we started with.

First, I show you a graphical depiction of what these linear combinations would look like when each atomic orbital is considered in isolation.

As you can see, the A and B irreps each pertain to a single linear combination, while the degenerate E irreps pertain to two.

Finally, I want to show you what these would look like if the vector fields associated with each orbitals were added up to then construct the molecular isosurface:

Though in practice the coefficients used on each atomic orbital would have been optimized for lowering electron repulsion, it is still interesting to see the shapes that arise from adding these fields of electron density and how they relate to the images I showed before.

Thank you very much for watching!

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But before ending this video I have a little treat for the more curious among you. Though I wont go into details, once the irreps are known, further processing can be done to find out which linear combinations of atomic orbitals would have the symmetries described by each irrep. These can be plotted to show the symmetries hidden in the our basis set.

Finally, we have the reflections across the vertical mirror planes. Since each plane cross two carbon atoms, each keeps two of them in place with unchanged orientation. Furthermore, since there is a total of 3 mirrors of reflections, this operation has a trace of 6.