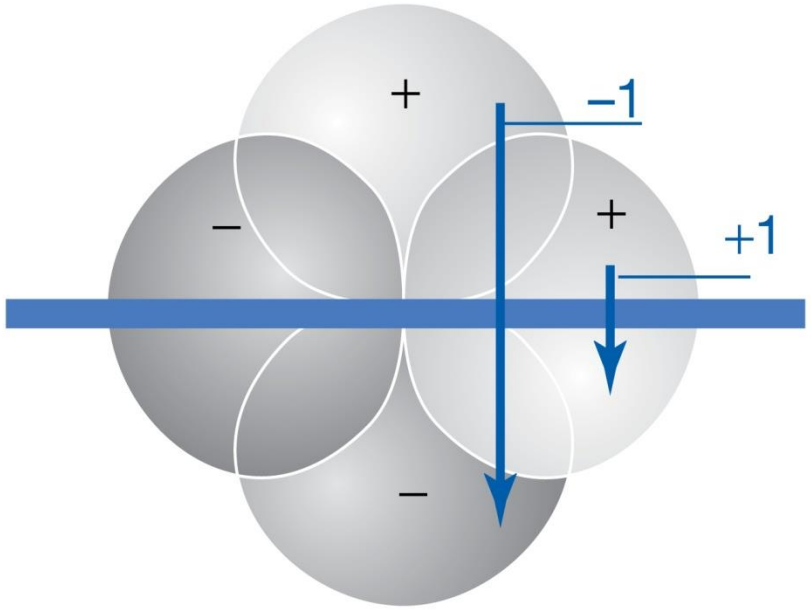
(d) Characters and operations

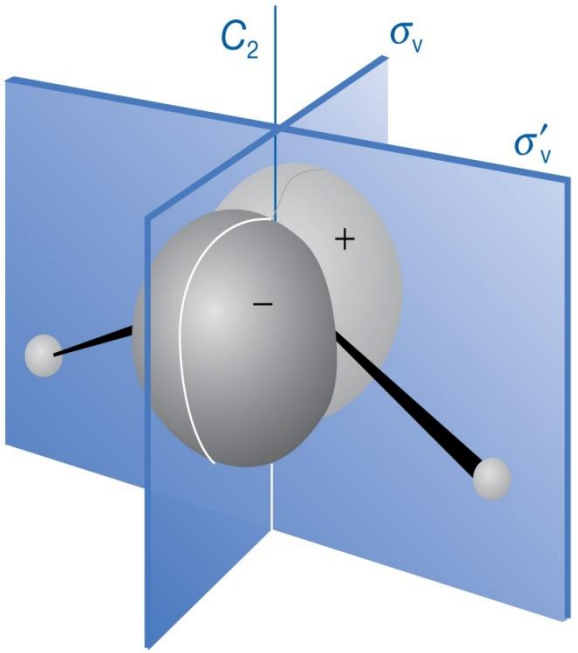
- We can identify the symmetry label of the orbital by comparing the changes that occur to an orbital under each operation, and then comparing the resulting +1 or −1 with the entries in a row of the character table for the point group concerned

- For the rows labelled E or T, the characters in a row of the table are the sums of the characters summarizing the behavior of the individual orbitals in the basis.
- Thus, if one member of a doubly degenerate pair remains unchanged under a symmetry operation but the other changes sign, then the entry is reported as $\chi = 1 - 1 = 0$.



The two orbitals shown here have different properties under reflection through the mirror plane: one change sign (Character −1); the other does not (character +1)

- Consider the O2p_x orbital in H_2O.
- the labels available for the orbitals are a_1, a_2, b_1 and b_2.
- Under a 180° rotation (C_2) the orbital changes sign, so it must be either B_1 or B_2 ($\chi = -1$)
- The O2p_x orbital also changes sign under the reflection, which identifies it as B_1
- Similarly, O2p_y changes sign under C_2 but not under σ_v' therefore, it can contribute to b_2 orbitals



- The behaviour of *s*, *p*, and *d* orbitals on a central atom under the symmetry operations of the molecule is so important that the symmetry species of these orbitals are generally indicated in a character table.
- We look at the symmetry species of *x*, *y*, and *z*.
- Thus, the position of *z* shows that p_z (which is proportional to *zf(r)*), has symmetry species A_1 (in C_{3v} Table)
- Whereas p_x and p_y (which are proportional to *xf(r)* and *yf(r)*, respectively) are jointly of E symmetry.

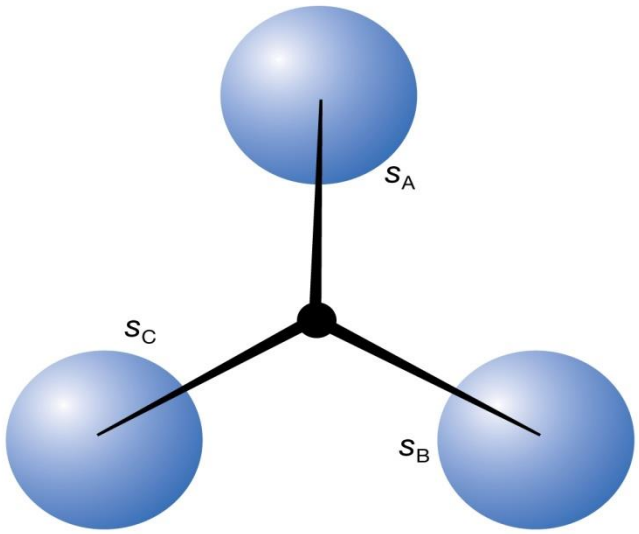
C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

- An *s* orbital on the central atom always spans the fully symmetrical irreducible representation of a group as it is unchanged under all symmetry operations.
- The five *d* orbitals of a shell are represented by *xy* for d_{xy}, etc. and are also listed on the right of the character table.
- We can see at a glance that in C_{3v}, d_{xy} and d_{x2-y2} on a central atom jointly belong to E and hence form a doubly degenerate pair

(e) The classification of linear combinations of orbitals

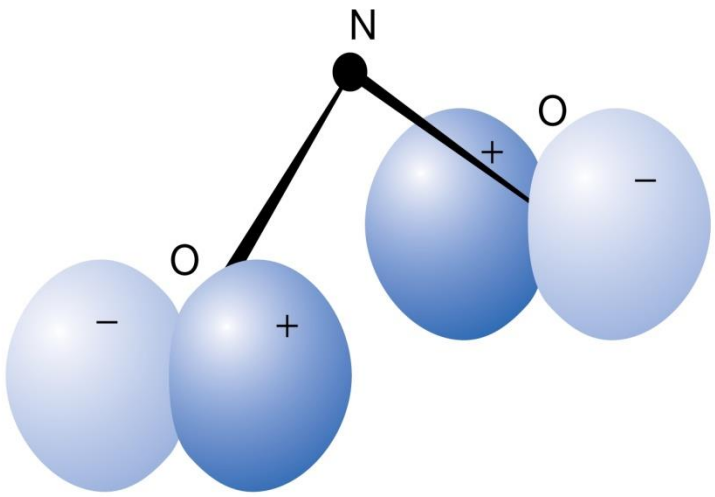
- The same technique may be applied to linear combinations of orbitals on atoms that are related by symmetry transformations of the molecule
- such as the combination $\psi_1 = \psi_A + \psi_B + \psi_C$ of the three H *1s* orbitals in the C_{3v} molecule NH_3.

- This combination remains unchanged under a C_3 rotation and under any of the three vertical reflections of the group, so its characters are:
- $\chi(E) = 1$ $\chi(C_3) = 1$ $\chi(\sigma_v) = 1$
- ψ_1 is of symmetry species A_1 and contributes to a_1 molecular orbitals in NH_3.
- $\psi_1 \sim a_1$



The three H *1s* orbitals used to construct symmetry-adapted linear combinations in C_{3v} molecule such as NH_3.

- Consider the orbital $\psi_1 = \psi_A - \psi_B$ in a C_{2v} NO_2 ion, where ψ_A is an O$2p_x$ orbital on one O atom and ψ_B that on the other O atom
- The characters under the symmetry operations are
- $\chi(E) = 1$ $\chi(C_2) = 1$
  $\chi(\sigma_v) = -1$ $\chi(\sigma'_v) = -1$
- $\psi_1 \sim a_2$



One symmetry-adapted linear combination of O$2p_x$ orbitals in the C_{2v} NO_2 ion

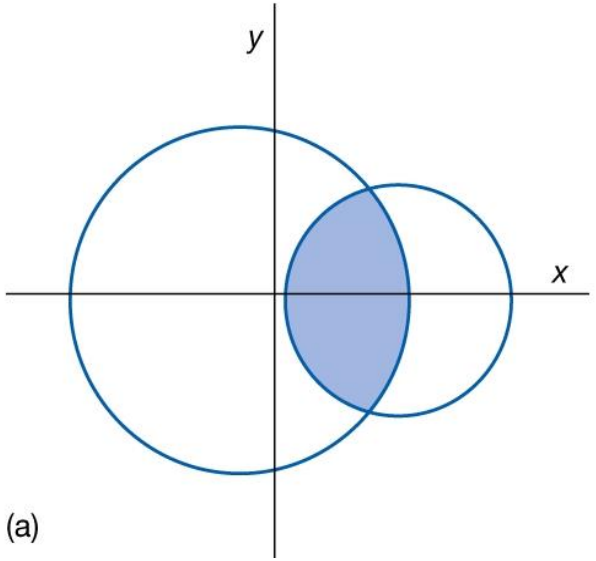
5 Vanishing integrals and orbital overlap

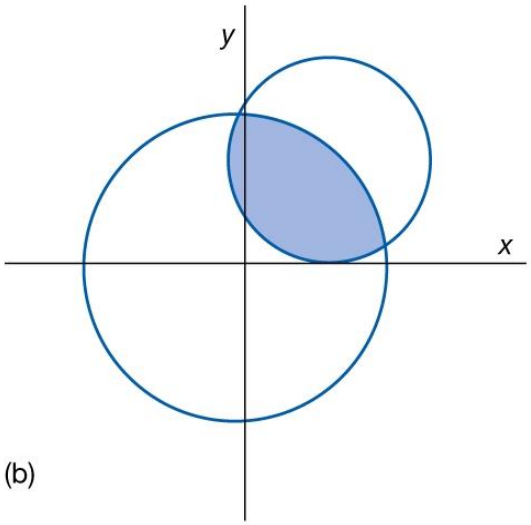
- Suppose we had to evaluate the integral

$$I = \int f_1 f_2 d\tau$$

- For example, f_1 might be an atomic orbital *A* on one atom and f_2 an atomic orbital *B* on another atom, in which case *I* would be their overlap integral.
- If we knew that the integral is zero, we could say at once that a molecular orbital does not result from *(A,B)* overlap in that molecule.

(a) The criteria for vanishing integrals





- The value of an integral *I* (for example, an area) is independent of the coordinate system used to evaluate it, as in the two choices shown in (a) and (b)

- The value of any integralis independent of the orientation of the molecule .
- In group theory we express this point by saying that *I is invariant under any symmetry operation of the molecule,* and that each operation brings about the trivial transformation $I \rightarrow I$.
- Because $d\tau$ is invariant under any symmetry operation, it follows that the integral is nonzero only if the integrand itself, the product $f_1 f_2$, is unchanged by any symmetry operation of the molecular point group.

- Therefore, for *I* not to be zero, *the integrand* $f_1 f_2$ *must have symmetry species* A_1 (or its equivalent in the specific molecular point group).
- If the integrand changed sign under a symmetry operation, the integral would be the sum of equal and opposite contributions, and hence would be zero.

- We use the following procedure to deduce the symmetry species spanned by the product $f_1 f_2$ and hence to see whether it does indeed span A_1
- 1 Decide on the symmetry species of the individual functions f_1 and f_2 by reference to the character table, and write their characters in two rows in the same order as in the table.
- 2 Multiply the numbers in each column, writing the results in the same order.
- 3 Inspect the row so produced, and see if it can be expressed as a sum of characters from each column of the group