



Part III Symmetry and Bonding

Chapter 4 Vanishing Integrals (零积分)

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4. Vanishing integrals



- One of the most powerful applications of *Group Theory* is the ability to decide whether a *particular integral* is *zero* or *not* without actually evaluating the integral.
- We will learn how this approach can be used to great advantage in *constructing molecular orbitals* and in *understanding spectroscopic selection rules*.
- For example, it is clear that the integral of the *even function is positive* but that of the *odd function must be zero*.
- Using *Group Theory* we can generalise this property of *odd* and *even functions* into a powerful method for deciding whether or not particular *integrals* will be *zero*.





4.1 Symmetry criteria for vanishing integrals



• Now consider the integral of a general function ψ over all space: $I = \int \psi d\tau$

 $I = \iiint_{-\infty}^{+\infty} \psi(x, y, z) dx dy dz \text{ (in cartesian coordinates)}$

- The *integrand* must transform as the *totally symmetric IR* to make the integral *non-zero*.
- If the *integrand* transforms as some other *IR*, the integral is *necessarily zero*.

The value of the integral $I = \int \psi d\tau$ is *necessarily zero* if ψ transforms as anything *other than the totally symmetric irreducible representation*.

• In other words, if ψ transforms as *a sum of IRs* that contain the totally symmetric *IR*, the integral is not necessarily zero.



4.2 Overlap integrals

• A commonly encountered integral in quantum mechanics, and especially when constructing MOs, is the *overlap integral* between two wavefunctions ψ_i and ψ_j ,

$$S_{ij} = \int \psi_i^* \psi_j d\tau$$

In H₂, the *overlap* of two 1s AOs centred on different atoms (1s(A) and 1s(B)):







4.2 Overlap integrals



- Suppose that ψ_i transforms as the $IR \Gamma^{(i)}$ and ψ_j transforms as $\Gamma^{(j)}$. Thus $\psi_i^* \psi_j$ transforms as $\Gamma^{(i)} \bigotimes \Gamma^{(j)}$.
- For the overlap integral to be *non-zero* the product Γ⁽ⁱ⁾ ⊗ Γ^(j) must be (or at least contains) the totally symmetric IR.
- The only way for the product $\Gamma^{(i)} \otimes \Gamma^{(j)}$ to contain the *totally symmetric IR* is for $\Gamma^{(i)}$ and $\Gamma^{(j)}$ to be the same. This leads to a very important conclusion about the overlap integral:

The overlap integral $S_{ij} = \int \psi_i^* \psi_j d\tau$ is non-zero only if ψ_i and ψ_j transform as the same *IR*. (i.e., '*symmetry compatible*'!)







• *Example*: the overlap between an *s* orbital and a p_x orbital (the internuclear axis is *z*).



- *Qualitative picture*: The overlap of the two positive parts of the wavefunctions (*positive overlap*) is cancelled by the *'negative overlap'* between the positive and negative parts of the wavefunctions.
- Symmetry argument: The s orbital is symmetric with respect to a mirror plane coming out of the plane of the paper whereas *the p_x orbital is anti-symmetric*. The two AOs do NOT have the same symmetry and therefore do not overlap.



More practical example

Figure out the symmetry-compatible overlap of AOs in OH:

- OH belongs to C_{∞} point group.
- Simple inspection:

H 1s ~
$$\Sigma^+$$
 (A₁) — O 2s ~ Σ^+ (A₁) \longrightarrow Symmetry compatible $A_1 \otimes A_1 = A_1$
O 2p_z ~ Σ^+ (A₁) \longrightarrow Symmetry compatible $O(2p_x, 2p_y) \sim \Pi(E_1) \longrightarrow$ Symmetry incompatible! $A_1 \otimes E_1 = E_1$

$\mathcal{C}_{\infty V}$		Ε	$2C^{z}(\alpha)$	•••	$\infty \sigma_v$			
Σ^+ (A ₁))	1	1	•••	1	Z		$x^2 + y^2; z^2$
Σ^- (A ₂))	1	1	•••	-1		R_z	
Π (E ₁))	2	$2\cos\alpha$	•••	0	(x,y)	(R_x, R_y)	(xz,yz)
Δ (E ₂))	2	$2\cos 2\alpha$	•••	0		2	$(x^2 - y^2, 2xy)$
Φ (E ₃))	2	$2\cos 3\alpha$	•••	0			
•••		•••	•••	•••	•••			



→ Z

O--H —



4.3 Matrix elements



• Another very commonly encountered *integral* in quantum mechanics is:

 $Q_{ij} = \int \psi_i^* \widehat{Q} \psi_j d\tau$

 \hat{Q} is a quantum mechanical operator. Q_{ij} is often described as a *matrix element*. The size of the matrix is determined by the number of basis functions ψ_i we choose to use.

- Apparently, Q_{ij} is of course just a number (scalar).
- To make the integral *non-zero*, the integrand (or part of it) must transform as *the totally symmetric representation*.
- Accordingly we need to work out the *triple direct product*: $\Gamma^{(i)} \otimes \Gamma^{(Q)} \otimes \Gamma^{(j)}$

where $\Gamma^{(i)}$, $\Gamma^{(j)}$ and $\Gamma^{(Q)}$ are the *IR*s of ψ_i , ψ_j , and \hat{Q} , respectively.



- Atomic orbitals (AOs) can overlap to form molecular orbitals (MOs).
- In the simplest molecule, H_2 , the 1s AOs of two H atoms can overlap to give

energy

i) an in-phase combination

- the bonding MO

ii) an out-of-phase combination

- the antibonding MO.

The **bonding MO** is lower in energy than the AOs, and the **antibonding** energy is higher.











- The MOs were generally written as a linear combination of the 1s AOs s_a and s_b on the different atoms: $\psi = c_a s_a + c_b s_b$ (for H₂, $|c_a| = |c_b|$, why?)
- The resulting energies of the MOs were:

 $E = \alpha \pm \beta$ [+ for *the bonding MO*, - for *the antibonding MO*].

• The quantities α and β are both energies, and are defined via the integrals:

 $\alpha = \int s_a \widehat{H} s_a d\tau = \int s_b \widehat{H} s_b d\tau$; $\beta = \int s_a \widehat{H} s_b d\tau = \int s_b \widehat{H} s_a d\tau$; both α and β are negative.

 \hat{H} is just the *Hamiltonian* for the electron and β is sometimes called the *resonance integral*.





energy = $\alpha - \beta$

1*s*

i energy = $\alpha + \beta$

note: β is

antibonding

1*s*

bonding

- The quantity β can be thought of as a measure of *the energy of interaction* between *the nuclei of both atoms* and the *electron density* arising from the *overlap* of the orbitals.
- *The larger* (more negative) β becomes, *the stronger the bond*.
- If β is zero, so there is no energetic advantage to forming a bond.







- These integrals are clearly matrix elements, and will only be *non-zero* if the result of *the triple direct product* $\Gamma^{(i)} \otimes \Gamma^{(\widehat{H})} \otimes \Gamma^{(j)}$ contains *the totally symmetric IR*.
- The *Hamiltonian* represents the energy of the system, and that this energy is a just a number (a scalar). That is, $\Gamma^{(\widehat{H})}$ must be *the totally symmetric IR*. So

 $\Gamma^{(i)} \otimes \Gamma^{(\widehat{H})} \otimes \Gamma^{(j)} = \Gamma^{(i)} \otimes \Gamma^{tot. sym.} \otimes \Gamma^{(j)} = \Gamma^{(i)} \otimes \Gamma^{(j)}.$

This product will only be equal to *the totally symmetric* **IR** if $\Gamma^{(i)} = \Gamma^{(j)}$.

The integral in $\int \psi_i^* \widehat{H} \psi_j d\tau$ will only be non-zero if $\Gamma^{(i)} = \Gamma^{(j)}$, i.e. the two wavefunctions transform as the same IR.





• This leads to the following result, which is exceptionally important when it comes to constructing MO diagrams:

MOs will only form between orbitals which transform as *the same IR*.

- In other words, 'only orbitals with *the same symmetry*, meaning that they transform as *the same IR*, will interact to form MOs'.
- So we will put this key result to good use right away.





1. The value of the integral $I = \int \psi d\tau$ is necessarily *zero* if ψ transforms as anything other than *the totally symmetric irreducible representation*.

2. The overlap integral $S_{ij} = \int \psi_i^* \psi_j d\tau$ is necessarily *zero* if ψ_i and ψ_j transform as different *IRs*. i.e. only wavefunctions with the same symmetry (meaning that they transform as the same *IR*) overlap.

3. The matrix element $Q_{ij} = \int \psi_i^* \hat{Q} \psi_j d\tau$, will necessarily be *zero* unless the result of the direct product $\Gamma^{(i)} \otimes \Gamma^{(Q)} \otimes \Gamma^{(j)}$ contains *the totally symmetric IR*.

4. MOs will only form between orbitals which transform as the same IR.