Part III Symmetry and Bonding

Chapter 4 Vanishing Integrals

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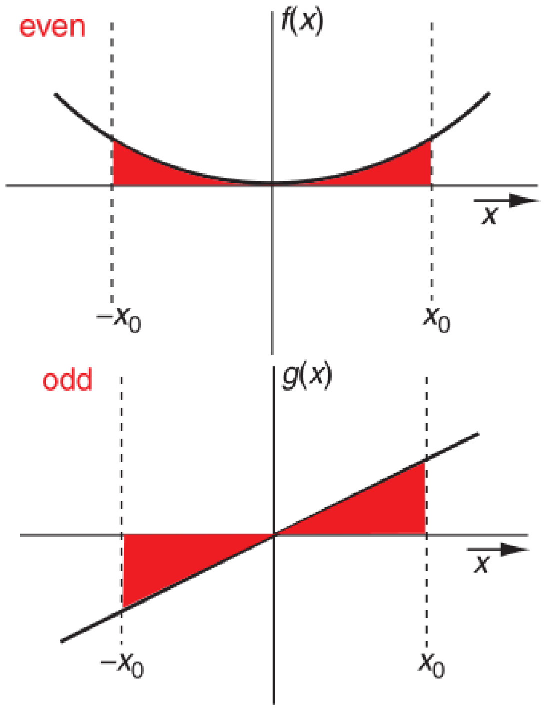
4. Vanishing integrals

- 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: $I = \int \psi d\tau$

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

- 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***.

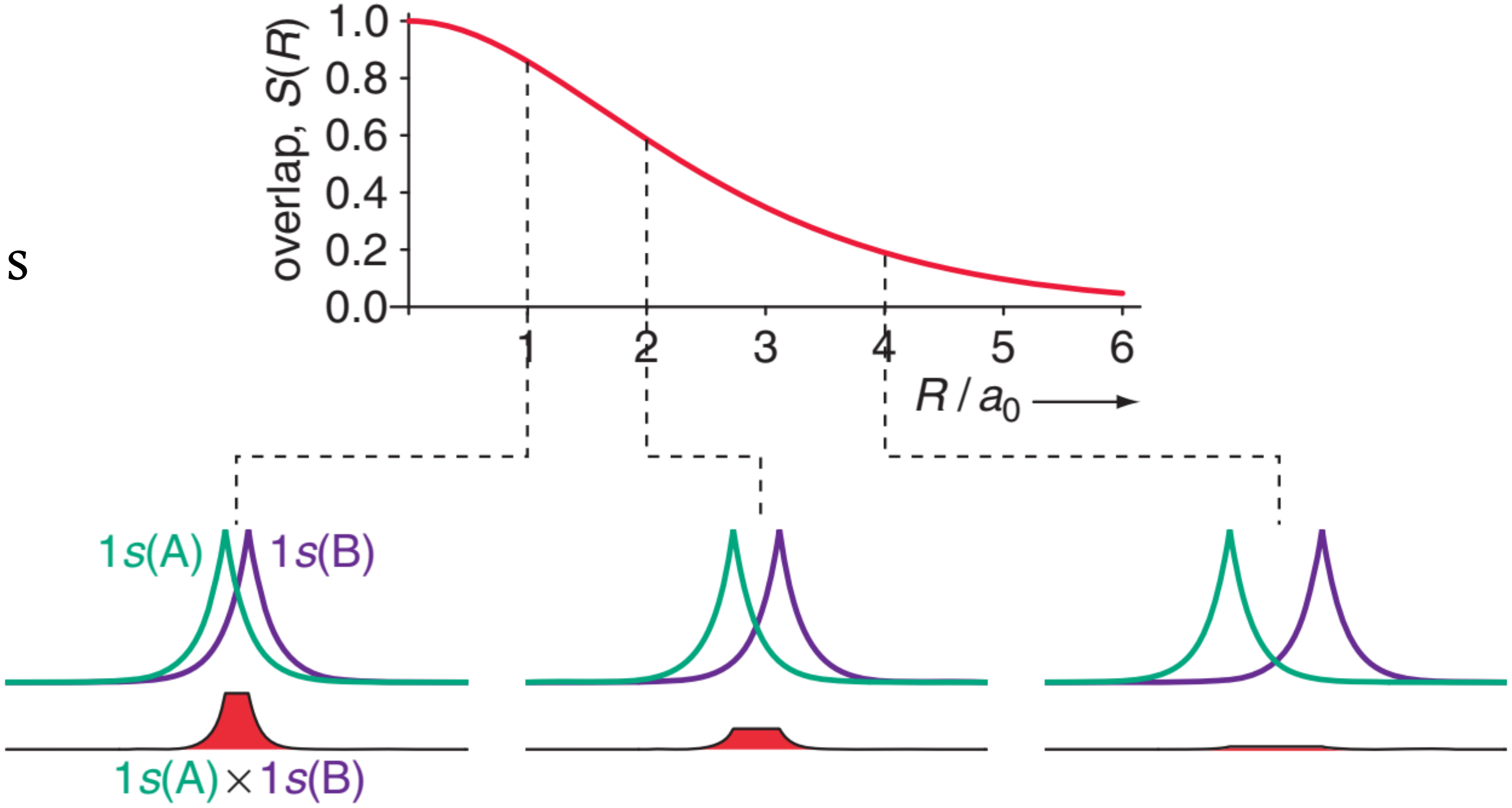
- In other words, if ***ψ*** transforms as ***a sum of IRs*** that contain the totally symmetric ***IR***, the integral is not necessarily zero.

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 H_2, the ***overlap*** of two 1s AOs centred on different atoms (1s(A) and 1s(B)):



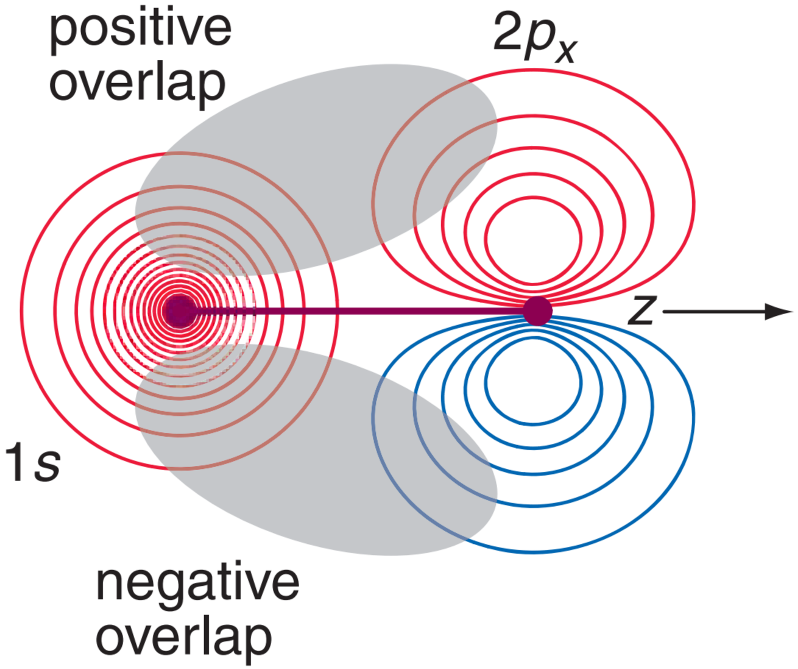
4.2 Overlap integrals

- Suppose that ψ_i transforms as the *IR* $\Gamma^{(i)}$ and ψ_j transforms as $\Gamma^{(j)}$. Thus $\psi_i^* \psi_j$ transforms as $\Gamma^{(i)} \otimes \Gamma^{(j)}$.
- For the overlap integral to be ***non-zero*** the product $\Gamma^{(i)} \otimes \Gamma^{(j)}$ ***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*')

4.2 Overlap integrals

- *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

O--H $\longrightarrow$ z

Figure out the symmetry-compatible overlap of AOs in OH: H 1s vs. O 2s, $2p_z$, $2p_x$, $2p_y$

- OH belongs to $C_{\infty v}$ point group.
- Simple inspection：

H 1s ~ $\Sigma^+ (A_1)$ — O 2s ~ $\Sigma^+ (A_1)$ $\longrightarrow$ ***Symmetry compatible*** $A_1 \otimes A_1 = A_1$

O $2p_z$ ~ $\Sigma^+ (A_1)$ $\longrightarrow$ ***Symmetry compatible***

O ($2p_x$, $2p_y$) ~Π (E_1) $\longrightarrow$ ***Symmetry incompatible!*** $A_1 \otimes E_1 = E_1$

$C_{\infty v}$	E	$2C^z(\alpha)$	$\cdots$	$\infty\sigma_v$			
Σ^+ (A_1)	1	1	$\cdots$	1	z		$x^2+y^2; z^2$
Σ^- (A_2)	1	1	$\cdots$	-1		R_z	
Π (E_1)	2	$2\cos\alpha$	$\cdots$	0	(x,y)	(R_x,R_y)	(xz,yz)
Δ (E_2)	2	$2\cos 2\alpha$	$\cdots$	0			$(x^2-y^2, 2xy)$
Φ (E_3)	2	$2\cos 3\alpha$	$\cdots$	0			
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$			

4.3 Matrix elements

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

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

$\hat{Q}$ 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.

4.3.1 Interactions leading to the formation of MOs

- *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

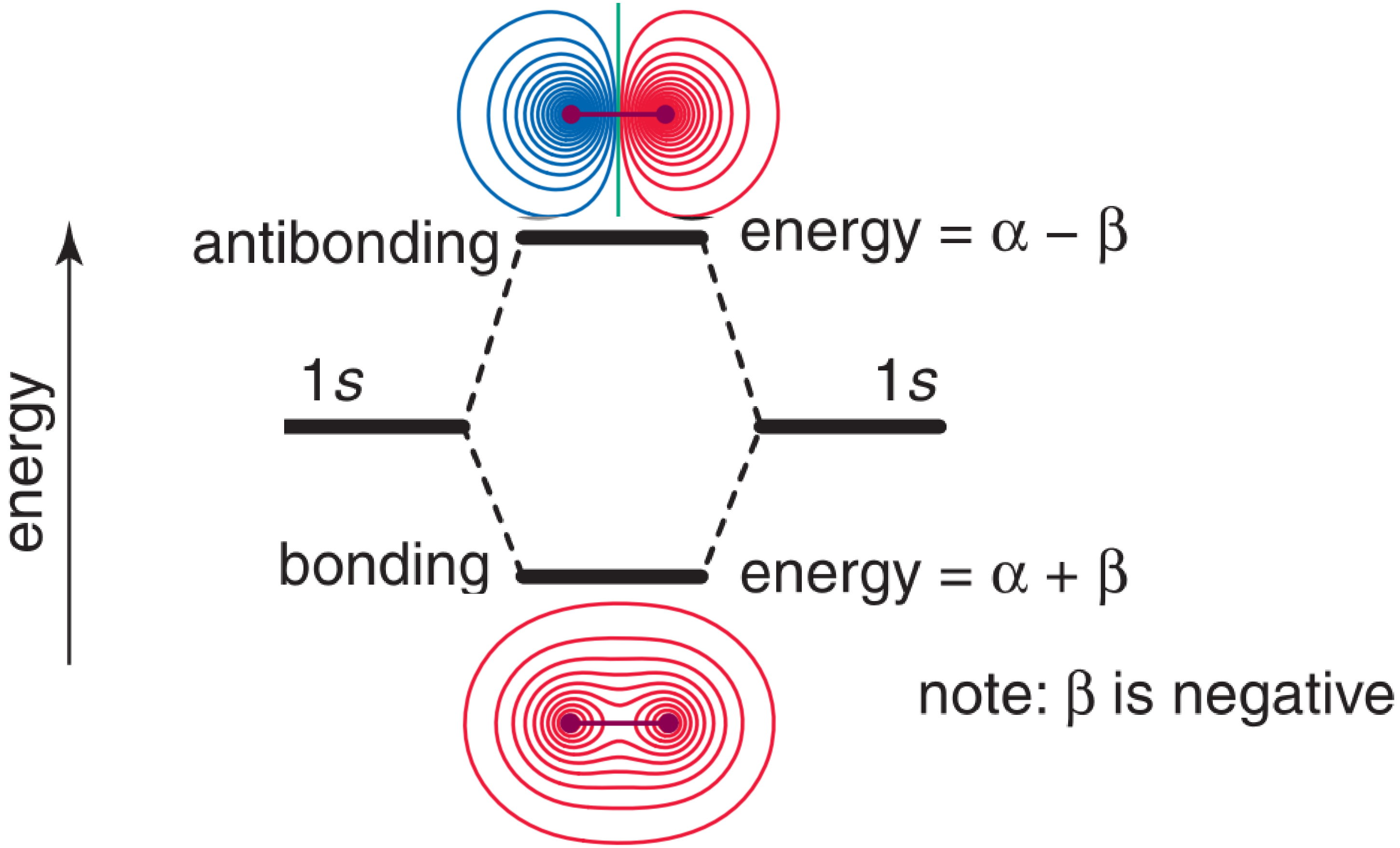
i) an in-phase combination

– 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.



4.3.1 *Interactions leading to the formation of MOs*

- 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 H_2, $|c_a| = |c_b|$, why?)

- The resulting energies of the MOs were:

$$E = \alpha \pm \beta$$

[+ for ***the bonding MO***, - for ***the antibonding MO***].

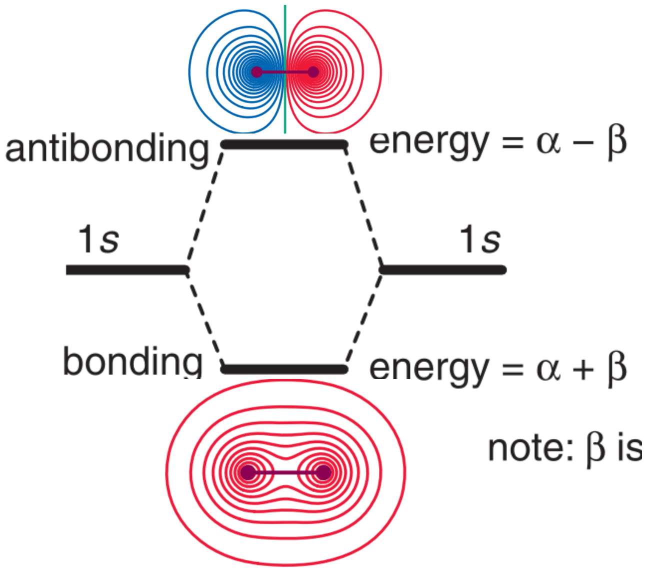
- The quantities α and β are both energies, and are defined via the integrals:

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

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

4.3.1 Interactions leading to the formation of MOs

- 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.



- For more complex molecules, quantities similar to ***β*** can be generally computed from integrals of the form:

$$\int \psi_i^* \hat{H} \psi_j \, d\tau$$

4.3.1 Interactions leading to the formation of MOs

- These integrals are clearly matrix elements, and will only be *non-zero* if the result of ***the triple direct product*** $\Gamma^{(i)} \otimes \Gamma^{(\hat{H})} \otimes \Gamma^{(j)}$ 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, $\Gamma^{(\hat{H})}$ must be ***the totally symmetric IR.*** So

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

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

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

4.3.1 Interactions leading to the formation of MOs

- 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.

4.4 Summary

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 *IR*s. 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***.