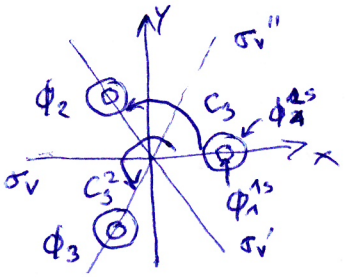
Tutorial: LCAO-MO method for H_3^{2+}

- it is the abbreviation for „linear combination of atomic orbitals – molecular orbitals"
- for simplicity, we will consider only 1s and 2s orbitals and the configuration of nuclei (protons) in the shape of the equilateral triangle



- in the basis of 6 atomic orbitals

$$\{\phi_i^{1s}\}_{i=1}^{3} \quad \text{and} \quad \{\phi_i^{2s}\}_{i=1}^{3},$$

we denote the matrix elements of the Hamiltonian H as (we assume C_{3v} symmetry)

$$\langle \phi_i^{ks} | H | \phi_j^{ks} \rangle = \begin{cases} \alpha_k & \text{for } i=j \\ \beta_k & \text{for } i \neq j \end{cases}$$

and

$$\langle \phi_i^{ks} | H | \phi_j^{ls} \rangle = \begin{cases} \gamma & \text{for } i=j,\ k \neq l \\ \delta & \text{for } i \neq j,\ k \neq l \end{cases}$$

here we assume that all functions are real and thus it is not necessary to use complex conjugation

- we get a full matrix representing H in this basis

$$H = \left(\begin{array}{ccc|ccc} \alpha_1 & \beta_1 & \beta_1 & \gamma & \delta & \delta \\ \beta_1 & \alpha_1 & \beta_1 & \delta & \gamma & \delta \\ \beta_1 & \beta_1 & \alpha_1 & \delta & \delta & \gamma \\ \hline \gamma & \delta & \delta & \alpha_2 & \beta_2 & \beta_2 \\ \delta & \gamma & \delta & \beta_2 & \alpha_2 & \beta_2 \\ \delta & \delta & \gamma & \beta_2 & \beta_2 & \alpha_2 \end{array}\right)$$

and also the overlap matrix

$$S = \left(\begin{array}{ccc|ccc} 1 & s_1 & s_1 & 0 & t & t \\ s_1 & 1 & s_1 & t & 0 & t \\ s_1 & s_1 & 1 & t & t & 0 \\ \hline 0 & t & t & 1 & s_2 & s_2 \\ t & 0 & t & s_2 & 1 & s_2 \\ t & t & 0 & s_2 & s_2 & 1 \end{array}\right)$$

since the atomic orbitals placed on different nuclei are not in general orthogonal (but we assume that they are orthonormalized on the same nucleus $\Rightarrow$ 1's and 0's)

- eigenstates and eigenenergies are then determined by solving time-independent Schrödinger equation $H\psi_i = E_i \psi_i$ which in the basis $\phi_1 = \phi_1^{1s}, \phi_2 = \phi_2^{1s}, \dots, \phi_6 = \phi_3^{2s}$ can be rewritten as ($\psi_i = \sum_{n=1}^{6} c_{in} \phi_n$ and we project it to $\langle \phi_m |$)

$$\sum_{n=1}^{6} (H_{mn} - E_i S_{mn})\, c_{in} = 0$$

- this is a generalized problem of eigenvalues that has a non-trivial solution for energies given by the condition

$$\det(H - ES) = 0$$

- instead of diagonalization of this 6×6 matrix, it is advantageous to use the symmetry of the system
- we will use only the subgroup $C_{3v} \subset D_{3h}$ because 1s orbitals do not change when σ_h is applied to them and thus it is not necessary to consider the full group D_{3h}
- as we will see later, the eigenstates of H form a basis to irreducible representations of the symmetry group a thus it is more simple to find them in the symmetrized basis

- when C_{3v} acts on 1s orbitals, they mix among each other, and independently also 2s orbitals, therefore we demonstrate the symmetrization process on the triple of basis functions ϕ_1, ϕ_2, ϕ_3 (e.g. 1s orbitals) satisfying

$$T(g)\phi_i = \sum_{j=1}^{3} \phi_j D^s_{ji}(g) \quad \text{for all } g \in C_{3v}$$

where the matrices $D^s(g)$ express how the s-orbitals are transformed among each other for elements of C_{3v}, particularly the column i of this matrix determines to what linear combination is transformed the orbital ϕ_i

- we get matrices (just look what happens at the figure)

$$D^s(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D^s(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad D^s(C_3^2) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

- e.g. ϕ_1 is transformed to ϕ_2 under C_3 etc.

$$D^s(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad D^s(\sigma_v') = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad D^s(\sigma_v'') = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- one can easily check that all these matrices commute with the submatrix of H of the type $\begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$ demonstrating thus its C_{3v} symmetry (which we assumed)

- the whole 6×6 matrix commutes with 6×6 matrices where 1s and 2s orbitals do not mix given by

$$D^{1s,2s}(g) = \begin{pmatrix} D^s(g) & 0 \\ 0 & D^s(g) \end{pmatrix}$$

- three basis functions ϕ_1, ϕ_2, ϕ_3 (1s or 2s orbitals) form a basis of a reducible representation of C_{3v} and using characters, we can decompose it into IRs of C_{3v},

- from the matrices we get

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ^s	3	0	1

but to obtain this character, it was not necessary to construct these matrices if we realize that

1) if an atom is displaced under the symmetry operation (e.g. under C_3, they are all displaced) then the corresponding orbital does not contribute to the character (0 on diagonal)
2) if an atom stays at the same place then the 1s orbital always contributes by 1 (p, d, ... orbitals contribute in the same way as they would be at the origin)

- using the character table for the group C_{3v} we easily find

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ^s	3	0	1

decomposition $\Gamma^s = A_1 \oplus E$

but in general we can use the formula

$$\alpha_\mu = \frac{1}{\#G} \sum_{k=1}^{N_c} n_k \chi^\mu(C_k)^* \chi(C_k)$$

to determine how many times a certain IR Γ^μ appears in the reduc. repr. with the character $\chi(C_k)$

- we can check that

$$\alpha^s_{A_1} = \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot 1\cdot 1) = 1$$

$$\alpha^s_{A_2} = \frac{1}{6}(1\cdot 1\cdot 3 + 2\cdot 1\cdot 0 + 3\cdot(-1)\cdot 1) = 0$$

$$\alpha^s_{E} = \frac{1}{6}(1\cdot 2\cdot 3 + 2\cdot(-1)\cdot 0 + 3\cdot 0\cdot 1) = 1$$

- the whole 6-dim. red. repr. $\Gamma^{1s,2s}$ then has decomposition

$$\Gamma^{1s,2s} = 2A_1 \oplus 2E$$

as 1s and 2s orbitals transform in the same way

- to construct the symmetrized basis, we can use the symmetrization (or projection) operators,
in the case of one-dimensional IRs, the situation is simple and we just use the projection operator $P^{\mu} = \frac{d_\mu}{\#G} \sum_{g \in G} \chi^{\mu}(g)^* T(g)$

giving for A_1

$$P^{A_1}\phi_1 = \frac{1}{6}\left(\overset{E}{1}\cdot\phi_1 + \overset{C_3}{1}\cdot\phi_2 + \overset{C_3^2}{1}\cdot\phi_3 + \overset{\sigma_v}{1}\cdot\phi_1 + \overset{\sigma_v'}{1}\cdot\phi_3 + \overset{\sigma_v''}{1}\cdot\phi_2\right) = \frac{1}{3}(\phi_1+\phi_2+\phi_3)$$

which is a completely-symmetric combination of 1s (or 2s) orbitals

- to get an orthogonalized basis for IR E, we need matrices representing the elements of C_{3v} in this representation, such as, for example, matrices from the action of C_{3v} in (x,y) plane

$$D^E(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D^E(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \quad D^E(C_3^2) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$D^E(\sigma_v) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad D^E(\sigma_v') = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \quad D^E(\sigma_v'') = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

$\sigma_v'' = \sigma_v \cdot C_3$, $\sigma_v'' = \sigma_v' \cdot C_3^2$

then we can use the symmetrization operators

$$P^{\mu}_{jk} v = \frac{d_\mu}{\#G} \sum_{g \in G} D^{\mu}_{jk}(g)^* T(g) v,$$

for $k=1$ and $v=\phi_1$ we have

$$P^E_{11}\phi_1 = \frac{2}{6}\left(\overset{E}{\phi_1} - \overset{C_3}{\tfrac{1}{2}\phi_2} - \overset{C_3^2}{\tfrac{1}{2}\phi_3} + \overset{\sigma_v}{\phi_1} - \overset{\sigma_v'}{\tfrac{1}{2}\phi_3} - \overset{\sigma_v''}{\tfrac{1}{2}\phi_2}\right) = \frac{1}{3}(2\phi_1 - \phi_2 - \phi_3)$$

$$P^E_{21}\phi_1 = \frac{2}{6}\left(\overset{E}{0\cdot\phi_1} + \overset{C_3}{\tfrac{\sqrt{3}}{2}\phi_2} - \overset{C_3^2}{\tfrac{\sqrt{3}}{2}\phi_3} + \overset{\sigma_v}{0\cdot\phi_1} - \overset{\sigma_v'}{\tfrac{\sqrt{3}}{2}\phi_3} + \overset{\sigma_v''}{\tfrac{\sqrt{3}}{2}\phi_2}\right) = \frac{1}{\sqrt{3}}(\phi_2 - \phi_3)$$

- if we have only the characters of IRs then we can use the incomplete projection operator P^{μ} on more basis functions and then orthogonalize them

$$P^E\phi_1 = \frac{2}{6}\left(\overset{E}{2\phi_1} - \overset{C_3}{1\cdot\phi_2} - \overset{C_3^2}{1\cdot\phi_3} - \overset{\sigma}{0}\right) = \frac{1}{3}(2\phi_1 - \phi_2 - \phi_3)$$

and similarly

$$P^E\phi_2 = \frac{1}{3}(2\phi_2 - \phi_3 - \phi_1), \quad P^E\phi_3 = \frac{1}{3}(2\phi_3 - \phi_1 - \phi_2)$$

- all these functions are orthogonal to $P^{A_1}\phi_1$, but they are not linearly independent and orthogonal $\Rightarrow$ Gram-Schmidt orthogonalization

- finally, we have to normalize the obtained functions

giving (up to overlaps, see below)

$$P^{A_1}\phi_1^{1s} \to \psi_1^{A_1} = \frac{1}{\sqrt{3}}\left(\phi_1^{1s}+\phi_2^{1s}+\phi_3^{1s}\right)$$

$$P_{11}^{E}\phi_1^{1s} \to \psi_2^{E} = \frac{1}{\sqrt{6}}\left(2\phi_1^{1s}-\phi_2^{1s}-\phi_3^{1s}\right)$$

$$P_{21}^{E}\phi_1^{1s} \to \psi_3^{E} = \frac{1}{\sqrt{2}}\left(\phi_2^{1s}-\phi_3^{1s}\right)$$

and similarly for 2s orbitals

$$\psi_4^{A_1} = \frac{1}{\sqrt{3}}\left(\phi_1^{2s}+\phi_2^{2s}+\phi_3^{2s}\right)$$

$$\psi_5^{E} = \frac{1}{\sqrt{6}}\left(2\phi_1^{2s}-\phi_2^{2s}-\phi_3^{2s}\right)$$

$$\psi_6^{E} = \frac{1}{\sqrt{2}}\left(\phi_2^{2s}-\phi_3^{2s}\right)$$

- one can easily check that functions belonging to different IRs are mutually orthogonal and the same is true also for pairs ψ_2^E and ψ_3^E or ψ_5^E and ψ_6^E that are transformed according to different columns of the matrix repr. E (later, we will prove this as a general result for matrix elements of invariant operators, here the operator is 1!)

- but if the symmetrized functions belong to the same IR then we get

$$\langle\psi_1^{A_1}|\psi_4^{A_1}\rangle = \frac{1}{3}\big(\overset{0}{\langle\phi_1^{1s}|\phi_1^{2s}\rangle} + \overset{t}{\langle\phi_1^{1s}|\phi_2^{2s}\rangle} + \overset{t}{\langle\phi_1^{1s}|\phi_3^{2s}\rangle} +$$
$$+ \overset{t}{\langle\phi_2^{1s}|\phi_1^{2s}\rangle} + \overset{0}{\langle\phi_2^{1s}|\phi_2^{2s}\rangle} + \overset{t}{\langle\phi_2^{1s}|\phi_3^{2s}\rangle} +$$
$$+ \overset{t}{\langle\phi_3^{1s}|\phi_1^{2s}\rangle} + \overset{t}{\langle\phi_3^{1s}|\phi_2^{2s}\rangle} + \overset{0}{\langle\phi_3^{1s}|\phi_3^{2s}\rangle}\big) = 2t$$

and similarly

$$\langle\psi_2^E|\psi_5^E\rangle = \langle\psi_3^E|\psi_6^E\rangle = -t$$

$$\langle\psi_1^{A_1}|\psi_1^{A_1}\rangle = 1+2s_1 \quad , \quad \langle\psi_2^E|\psi_2^E\rangle = \langle\psi_3^E|\psi_3^E\rangle = 1-s_1$$

$$\langle\psi_4^{A_1}|\psi_4^{A_1}\rangle = 1+2s_2 \quad , \quad \langle\psi_5^E|\psi_5^E\rangle = \langle\psi_6^E|\psi_6^E\rangle = 1-s_2$$

- in a similar way, we can evaluate the matrix elements of Hamiltonian in this basis, for example

$$\langle\psi_1^{A_1}|H|\psi_1^{A_1}\rangle = \frac{1}{3}(3\alpha_1+6\beta_1) = \alpha_1+2\beta_1$$
$$\langle\psi_1^{A_1}|H|\psi_2^{E}\rangle = 0 \quad \text{etc.}$$

- eigenenergies are then obtained using the determinant of the matrix

$$H^{\psi}-ES^{\psi} = \begin{pmatrix}
\alpha_1+2\beta_1-E(1+2s_1) & 0 & 0 & \gamma+2\delta-E2t & 0 & 0 \\
0 & \alpha_1-\beta_1-E(1-s_1) & 0 & 0 & \gamma-\delta-E(-t) & 0 \\
0 & 0 & \alpha_1-\beta_1-E(1-s_1) & 0 & 0 & \gamma-\delta-E(-t) \\
\gamma+2\delta-E2t & 0 & 0 & \alpha_2+2\beta_2-E(1+2s_2) & 0 & 0 \\
0 & \gamma-\delta-E(-t) & 0 & 0 & \alpha_2-\beta_2-E(1-s_2) & 0 \\
0 & 0 & \gamma-\delta-E(-t) & 0 & 0 & \alpha_2-\beta_2-E(1-s_2)
\end{pmatrix}$$

$\Rightarrow$ 3 independent terms for 2×2 submatrices for A_1 and twice for E

- instead of one 6×6 matrix, it is enough to diagonalize 2 matrices 2×2, because 2 matrices for the IR E (for pairs (ψ_2^E, ψ_5^E) and (ψ_3^E, ψ_6^E)) are the same

- if we would use only 1s orbitals, we would get directly a 3×3 matrix in the diagonal form (the first 3×3 part of the 6×6 matrix) and the eigenenergies are

$$E_1^{A_1} = \frac{\alpha_1 + 2\beta_1}{1+2S_1} \quad \text{for } \psi_1^{A_1}$$

$$E_{2,3}^{E} = \frac{\alpha_1 - \beta_1}{1-S_1} \quad \text{for } \psi_2^E \text{ and } \psi_3^E$$

} labelled according to the IRs of C_{3v}