Oxygen - 3 states

\[ y_2^x z \quad y^x z \quad x y z^2 \]

P state \( \ell = 1 \)

\[ M_L = \{ +1, 0, -1 \} \]

This is harder to deal with than real \( x, y, z \) functions

\[(x y - y x) \delta \]

\[ \cos \phi, \sin \phi_2 - \sin \phi_1, \cos \phi_2 = \sin (\phi_2 - \phi_1) \Rightarrow \text{This does not change with rotation about } x, M_L = 0 \]

Arbitrarily we'll call \( \{ y^2 x, M_L = +1 \} \) \( \{ y x^2, M_L = -1 \} \) rigorous.

\[ \{ x x x \theta y y \} \quad \{ x y x \beta x x \} \]

They transform the same way just like a pure \( x \) and a pure \( y \) would transform.

Using the Pauli principle we determine the symmetry of the spatial wave function and then substitute them in terms of trigonometric expressions and applying identities we evaluate the symmetry vs. rotation around \( \theta \) - axis.

\[
\begin{align*}
\ell = 1 & \quad \quad M_L = 0.5 \\
\ell = 2 & \quad \quad M_L = +1, -1, 0 \\
\ell = 3 & \quad \quad M_L = +2, -2, +1, -1, 0 \\
\ell = 4 & \quad \quad M_L = +3, -3, +2, -2, +1, -1, 0 \\
\ell = 5 & \quad \quad M_L = +4, -4, +3, -3, +2, -2, +1, -1, 0 \\
\end{align*}
\]
The terms Si,P,D, etc. came from the form of the trigonometric expression that described the product of the resulting wavefunction combinations and evaluating which orbital they resemble.

\[ \begin{align*}
\text{Rotation Around } z\text{-Axis} & \\
\text{11 Functions (1 sign change)} & \\
\text{5 Functions (2 sign changes)} & \\
\Sigma \text{ Functions (No sign change)} & \\
\end{align*} \]

\[ \text{Symmetry} \]

What operations leave the Hamiltonian unchanged.

i) \( C_{2z} \) (rotation around \( z \)-axis, 180°)
\[ C_{2z} = e^{i \pi} \text{ einheit} \]
\[ x \rightarrow -x \]
\[ y \rightarrow -y \]
\[ z \rightarrow z \]
\[ C_{2z} \psi = +\psi \text{ A symmetry} \]
\[ C_{2z} \psi = -\psi \text{ B symmetry} \]

ii) Mirror plane \( yz \) \( \Sigma_{yz} \)
\[ x \rightarrow -y \]
\[ y \rightarrow y \]
\[ z \rightarrow z \]
\[ \Sigma_{yz}^2 = e \]
\[ \Sigma_{yz} \psi = +\psi \]
\[ \Sigma_{yz} \psi = -\psi \]
We also have \( \sigma_{xz} \psi \rightleftharpoons -\psi \)

iii) Multiple operations

\[
\begin{align*}
\sigma_{xz} C_{2z}
\end{align*}
\]

\[
\begin{align*}
x \rightarrow x & \quad \rightarrow z \\
y \rightarrow -y & \quad \rightarrow -y \\
x \rightarrow -x & \quad \rightarrow z \\
y \rightarrow y & \quad \rightarrow y
\end{align*}
\]

\[
\Rightarrow \quad \sigma_{yz} = \sigma_{xz} C_{2z}
\]

Group = \{ e, C_{2z}, \sigma_{xz}, \sigma_{yz} \}

\[
\underbrace{\text{generators of the group}}_{\text{They aren't all independent.}}
\]

<table>
<thead>
<tr>
<th></th>
<th>( e )</th>
<th>( C_{2z} )</th>
<th>( \sigma_{xz} )</th>
<th>( \sigma_{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

Classification of wave functions based on the symmetry.

We pick the plane that causes the most changes upon application of the generator.

Consider water

\[
\sqrt{(\phi_{1s})^2 (\phi_{2s})^2 (OH_1)^2 (OH_2)^2 (O\Pi x)^2}
\]

\( \uparrow \) ORBITAL ON THE OXYGEN

\( \uparrow \) THIS BOND

What symmetry does it have
\[ \sum_{y^3} \psi = + \psi \]
\[ \sum_{x^3} \psi = + \psi \]

The only ones that change
\[ \sum (OH_2 \alpha)(OH_2 \beta)(OH_1 \alpha)(OH_1 \beta) \]
2 sign changes in the determinant
→ no net change

\[ \Rightarrow \sum_{x^3} \psi = + \psi \]

\[ \Rightarrow H_2O \text{ is an } ^1A_1 \text{ function.} \]

Consider now \[ N \begin{array}{c} H \\ H \end{array} \]

\[ \sum (\phi_1)^2 (\phi_2)^2 (OH_1)^2 (OH_2)^2 (O \Pi \alpha) \]

This is a \[ ^2B_1 \text{ state as we can easily verify.} \]

\[ \text{Carbon atom} \]
\[ \text{\begin{array}{c} s^2 \\ p_x \\ p_y \end{array}} \]

\[ \text{\begin{array}{c} s^2 + S \bar{z} S \bar{z} \end{array}} (\alpha \beta - \beta \alpha) \]

\[ SS = \chi^2 \pm \tau \]

\[ 0.16 \text{ NOT THAT MUCH P CHARACTER.} \]

\[ \text{\begin{array}{c} 2T \text{ STATE} \end{array}} \]

\[ \text{\begin{array}{c} 4 \Sigma^- \end{array}} \]
\( \text{Ne}_2 \)

\[ \sum^+ \]

\[ \forall (x\alpha)(x\beta)(y\alpha)(y\beta) \]

\[ x \rightarrow \cos \alpha \ x + \sin \alpha \ y \]
\[ y \rightarrow \cos \alpha \ y + (-\sin \alpha \ x) \]

\[ \rightarrow (\cos^2 \alpha + \sin^2 \alpha) \forall x^2y^2 \]

**Inversion symmetry**

\[ x \rightarrow -x \]
\[ y \rightarrow -y \]
\[ z \rightarrow -z \]

\[ I\Psi_g = +\Psi_g \]
\[ I\Psi_u = -\Psi_u \]

\[ I^2 = e \]

This molecule has \( g \) inversion symmetry. The only problem is that we have no bond.

**Ne\(_2^+\)**

\[ \sum^+ \]

**F\(_2\)**

\[ \sum^g \]

**O\(_2\)**

**Singlet**

---

This is better
\( \Sigma \) states can have + or - symmetry upon reflection over a plane.

Unpairing lobe orbitals costs energy:

<table>
<thead>
<tr>
<th>Bond Energy</th>
<th>Lobe</th>
</tr>
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<tbody>
<tr>
<td>P</td>
<td>80</td>
</tr>
<tr>
<td>CH</td>
<td>63</td>
</tr>
<tr>
<td>SiH</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>34</td>
</tr>
</tbody>
</table>

(Catalyzed to 2nd P)

\[ \text{CH}_2 \text{H}_2 \text{SiH}_2 \]

Bonding to both lobes:

\[ \text{CH}_2 \text{H}_2 \text{SiH}_2 \]

(For Si it is harder to form bonds using lobe orbitals)

Bonding the 'A', to another hydrogen:

H must come at the top or bottom \( \rightarrow \text{SiH}_3 \) is pyramidal

Bonding to 3B, another hydrogen \( \rightarrow \text{CH}_3 \) is planar

Flat curve