Orthogonality and Symmetry Projection Operators

The "Great Orthogonality Theorem States that the rows of characters are **orthogonal vectors.**

This allows one to project out any symmetry $\boldsymbol{\Gamma}$ from _**any**_ one of the basis functions, Φ :

$\Psi_\Gamma = \sum_1^n \chi_{\Gamma i} O_i \, \Phi$ (sum over sym. operators i from 1 to n)

where $= O_i$ is the ith symmetry operation,

  and $\chi_{\Gamma i}$ is the character for the ith operation of $\boldsymbol{\Gamma}$ symmetry.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_g	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

Note the orthogonality of the character rows.

(Be sure to include **ALL operators**, by noting the numbers preceding each operator in the top row.) For example: $<B_{2u}|E_{1u}>$:

(1)(2) + 2(-1)(1) + 2(1)(-1) + (-1)(-2) + 3(-1)(0) + 3(1)(0) + (-1)(-2) + 2(1)(-1) + 2(-1)(1) + (1)(2) + 3(1)(0) + 3(-1)(0)

= +2   -2   -2   +2   +0   +0   +2   -2   -2   +2   +0   +0

= 0

The x transition dipole integral, $\int\limits_{-\infty}^{\infty} \Psi_1 * \bar{x} \, \Psi_2 \, d\tau$

Example: operator x = E_{1u}, and ψ_1 is A_g ground state, then need $\psi_1 = E_{1u}$ i.e., **only transition to E_{1u} are dipole allowed. x and y are equivalent.**

EXAMPLE: C_3 for the 3 1s atomic orbitals (AOs) on the H atoms of the object shown. (Assume the point group is C_3 because the blue object in the center is more complicated that it looks.)

The C_3 character table is:

|	I	C_3^+	C_3^-
A	1	1	1
E	2	-1	-1
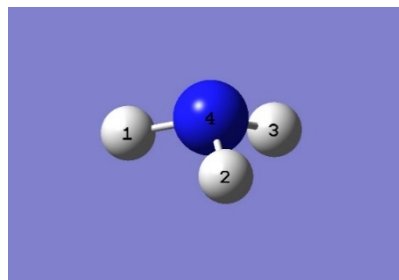
where I is the identity operator, C_3^+ is clockwise, and C_3^- is counter clockwise. Let the basis set be the 3 1s AOs: ϕ_1, ϕ_2, and ϕ_3 with orientation as shown.

1. Generate a linear combination from this basis set that has "A" symmetry, i.e., is a basis for the A irreducible representation.

$\Psi_A = \mathbf{1}I\,\phi_1 + \mathbf{1}C_3^+ \times \phi_1 + \mathbf{1}C_3^- \times \phi_1 = \phi_1 + \phi_2 + \phi_3$ (**characters** in **red**)

(The same result is obtained operating on ϕ_2 or ϕ_3, obviously.)

3

	I	C_3^+	C_3^-
A	1	1	1
E	2	-1	-1
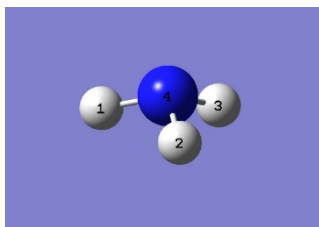
2. Generate a linear combination from this basis set that has "E" symmetry, i.e., is a basis for the E irreducible representation.

Because both the E and the character 2 for the Identity operation signify double degeneracy, we need to generate *two independent* linear combinations.

$$\Psi_{E1} = \mathbf{2}\, \boldsymbol{I}\, \phi_1 + (\mathbf{-1})\, \boldsymbol{C_3}^+ \phi_1 + (\mathbf{-1})\boldsymbol{C_3}^- \phi_1 = 2\, \phi_1 - \phi_2 - \phi_3$$

$$\Psi_{E2} = \mathbf{2}\, \boldsymbol{I}\, \phi_2 + (\mathbf{-1})\, \boldsymbol{C_3}^+ \phi_2 + (\mathbf{-1})\, \boldsymbol{C_3}^- \phi_2 = 2\, \phi_2 - \phi_3 - \phi_1$$

Not orthogonal

[If we operate on ϕ_3 we get $\Psi_{E3} = 2\, \phi_3 - \phi_1 - \phi_2$, but this not independent because $\Psi_{E3} = - (\Psi_{E1} + \Psi_{E2})$]

Now, we calculate the energies of these MO fragments in units of H_{12} by making an H matrix with $H_{11}=H_{22}=H_{33} = 0$ and $H_{12} = H_{13} = H_{23} = -1$ and use **Colby Diagonalizer**

$$\mathbf{H}= \begin{matrix} 0 & & \\ -1 & 0 & \\ -1 & -1 & 0 \end{matrix}$$
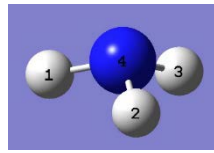
From Colby Diag.

Eigenvector 1: $E=1$

0.707107

-0.707107

0

Eigenvector 2: $E=1$

-0.408248

-0.408248

0.816497

Eigenvector 3: $E= -2$

0.57735

0.57735

0.57735

This tells you that Ψ_A is indeed a normalized version of $\phi_1 + \phi_2 + \phi_3$, and is the lowest energy. For Ψ_{E1} and Ψ_{E2} ,you indeed find the energy to be degenerate and much higher, as it should be because of antibonding.

One of the eigenvectors is $2\phi_3 - \phi_1 - \phi_2$, which looks like what we got operating on ϕ_3.

but **the other is $\phi_1 - \phi_2$. Where did that come from?**

Two hidden aspects that are common to programs that diagonalize symmetric matrices:

1) All eigenvectors are made orthogonal, even though this is not a requirement for degenerate eigenvectors.

2) I **_believe_** that Colby deliberately beutifies the eigenvectors by breaking the symmetry such that there is effectively a plane of symmetry going through atom 3 and bisecting the 1-2 bond. The eigenfuctions functions are perfect (to 5 decimal places) eigenfunctions for reflection through that plane with eigenvalues +1 and -1.

 This is not the case with all computers.

Colby with H$_{11}$ = 1 x 10^{-8}

Eigenvector 1: Eigenvalue=**1**
0.816497
-0.408248
-0.408248

Eigenvector 2: Eigenvalue=**1**
-1.67295e-8
-0.707107
0.707107

Eigenvector 3: Eigenvalue=**-2**
0.57735
0.57735
0.57735

Another diagonalizer on same matrix with **perfect symmetry gives these eigenvalues:**

-2.0000   1.0000   1.0000

and **eigenvectors:**

1	-.577350	.788133	-.213336
2	-.577350	-.578821	-.575875
3	-.577350	-.209312	.789212

The pair of degenerate eigenvectors are UGLY, but orthogonal.

You can show that they form a basis for the **E** irreducible representation, creating 2x2 representative matrices with trace =2, and have the correct multiplication properties.

You can *beautify* these ugly eigenvectors with **two** linear combinations that give: $2\phi_1 - \phi_2 - \phi_3$ and $\phi_2 - \phi_3$
That will be a future homework problem.

Born-Oppenheimer Approximation

Adiabatic Assumption: Nuclei move so much more slowly than electron that the electrons that the electrons are assumed to be obtained if the nuclear kinetic energy is ignored, i.e., solve for the electronic wavefunctions with stationary nuclei.

The complete molecular Hamiltonian (neglecting magnetic terms is:

$$H = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e}\sum_{i}\nabla_i^2 + \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}}$$

$$-\sum_{\alpha}\sum_{i}\frac{Z_{\alpha}e^2}{r_{i\alpha}} + \sum_{i}\sum_{j>i}\frac{e^2}{r_{ij}}$$

$$= T_N + T_e + V_{NN} + V_{Ne} + V_{ee}$$

Define $H_{el} = T_e + V_{Ne} + V_{ee}$

The *separation of time scales* allows the solution of $H_{el} \Psi_{el,n}(q_i;Q_\alpha)$ $=E_{el,n}(Q_\alpha)\Psi_{el,n}(q_i;Q_\alpha)$ at a set of fixed nuclear configurations, Q_α for the ground and excited states, n. Adding on the V_{NN} also a function of Q_α gives:

$U_n(Q_\alpha)= E_{el}(Q_\alpha) + V_{NN}(Q_\alpha)$, which serves the potential energy for the nuclei.

$U_n(Q_\alpha)$ are called Born-Oppenheimer potential (energy) surfaces.
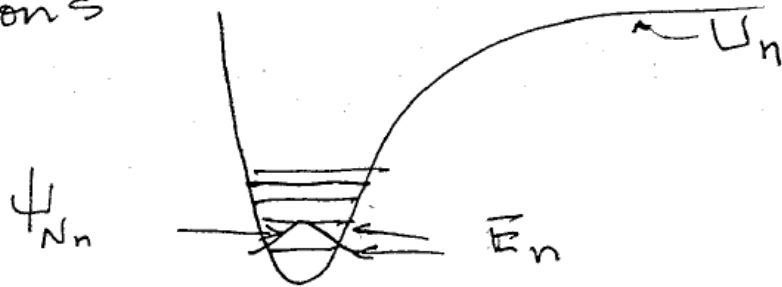
The $U_n(Q_\alpha)$ look like:
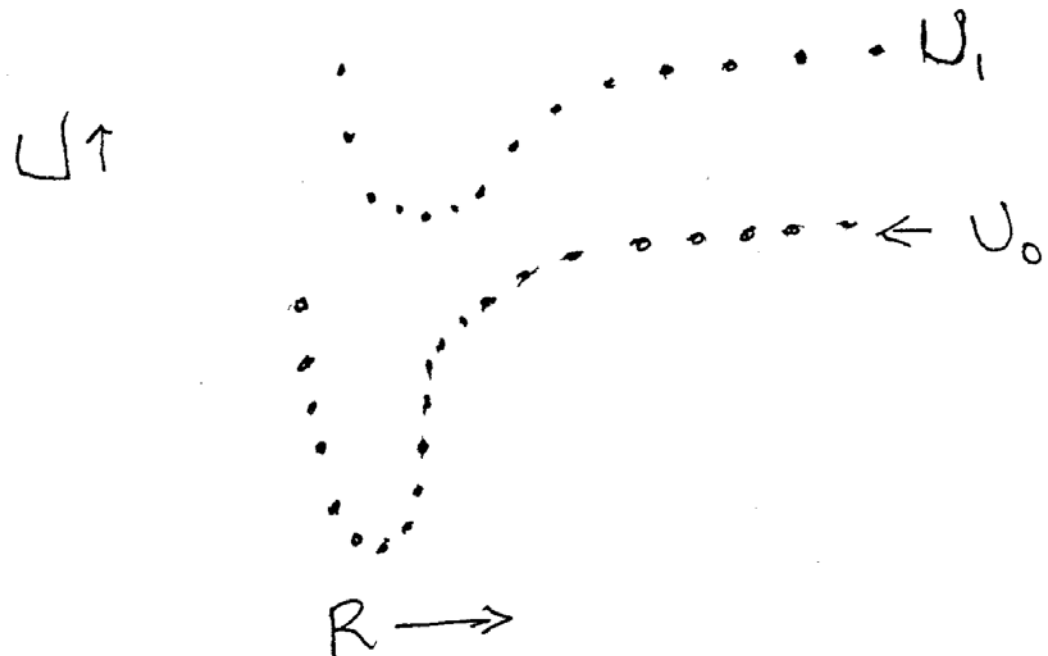
The $\ddot{U}_n(q_\alpha)$ are effective potential energy functions for the nuclear motion, to be used in the nuclear Schroedinger equation:

$$\mathcal{H}_N = T_N + U_n(q_\alpha) \qquad \mathcal{H}_N \psi_N(q_\alpha) = E_n \psi_N(q_\alpha)$$

The ψ_N are similar to harmonic oscillator wave functions

ψ_{Nn} $\overset{\frown}{} U_n$

E_n

One now defines the
nuclear Hamiltonian as $H_{Nn} = T_N + U_n(Q_\alpha)$
and solves the nuclear Schrodinger Equations on these surfaces:

$H_{Nn}\phi(Q_\alpha) = E_n\phi(Q_\alpha)$

The low energy solutions $\phi(Q_\alpha)$ will look very much like harmonic oscillator eigenfunctions:

$\Psi_{BO} = \Psi_{el,n}(q_i;Q_\alpha)\,\phi(Q_\alpha)$

The semicolon in $\Psi_{el,n}(q_i;Q_\alpha)$ means the electronic function depends only **parametrically** on Q_α (i.e., does not appear explicitly in $\Psi_{el,n}(q_i;Q_\alpha)$. It nevertheless depends very much on Q_α because the electron density follows the nuclei.