Hückel Theory

A plane molecule of n identical atoms has molecular orbitals (MOs) with energy levels $E_1 \leqslant \ldots \leqslant E_n$. Its graph has eigenvalues $\lambda_1 \geqslant \ldots \geqslant \lambda_n$, where

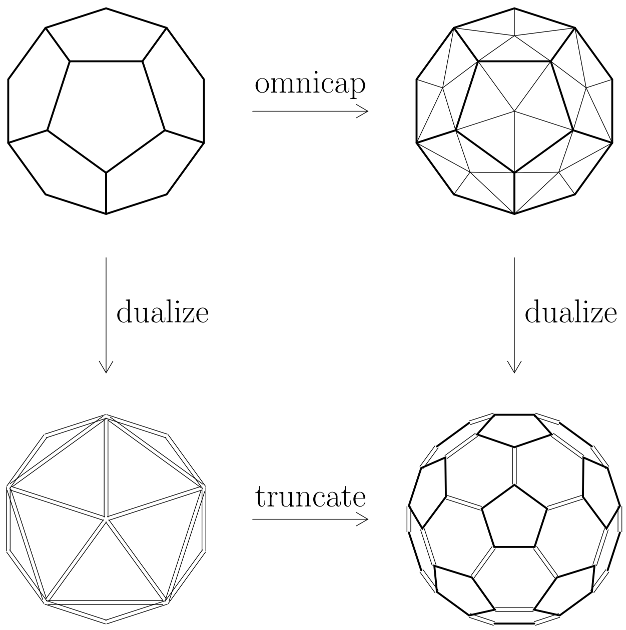
$$E_k = \alpha + \beta\lambda_k \quad (k = 1, \ldots, n;\ \ \beta < 0).$$

A MO is:	if it corresponds to:
occupied	$\lambda_1, \ldots, \lambda_{\frac{1}{2}n}$
unoccupied	$\lambda_{\frac{1}{2}n+1}, \ldots, \lambda_n$
highest occupied (HOMO)	$\lambda_{\frac{1}{2}n}$
lowest unoccupied (LUMO)	$\lambda_{\frac{1}{2}n+1}$
bonding	$\lambda_k > 0$
non-bonding	$\lambda_k = 0$
antibonding	$\lambda_k < 0$

A molecule is **closed shell** (chemically stable) if its HOMO is bonding and its LUMO is antibonding, i.e., $\lambda_{\frac{1}{2}n} > 0$ and $\lambda_{\frac{1}{2}n+1} < 0$.

The Leapfrog Operation

Polyhedron P



Leapfrog $L(P)$ or $\hat{P}$ of P

A **polyhedron** is a 3-connected planar graph.

A **fullerene** or **buckyball** is a (molecule represented by) a 3-regular polyhedron with only pentagonal and hexagonal faces.

A 3-regular polyhedron will always have n vertices and eigenvalues

$$3 = \lambda_1 \geqslant \lambda_2 \geqslant \ldots \geqslant \lambda_n \geqslant -3.$$

Theorem. The leapfrog $\hat{P}$ of a 3-regular polyhedron P has $\lambda_{\frac{1}{2}n} \geqslant 0$ and $\lambda_{\frac{1}{2}n+1} < 0$. If P has a face with $3k \pm 1$ vertices, then $\hat{P}$ has $\lambda_{\frac{1}{2}n} > 0$ and $\lambda_{\frac{1}{2}n+1} < 0$.

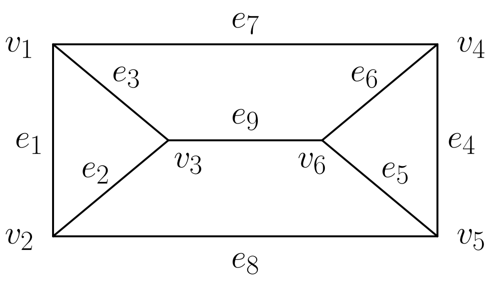
Corollary. Every leapfrog fullerene is closed shell.

It was originally conjectured that $\lambda_{\frac{1}{2}n} \geqslant 0$ for every fullerene, but a counterexample has since been found (with over 600 vertices!). However, it is still possible to conjecture:

Conjecture 1. $-0.02 < \lambda_{\frac{1}{2}n} \leqslant \frac{1}{2}(\sqrt{5} - 1)$ and $\lambda_{\frac{1}{2}n-1} \geqslant 0$ for every fullerene.

Conjecture 2. Most (which?) 3-regular polyhedra have $\lambda_{\frac{1}{2}n} \geqslant 0$ and $\lambda_{\frac{1}{2}n+1} \leqslant 0$.

If P is the dodecahedron (C_{20}), then $\lambda_{\frac{1}{2}n-1} = \ldots = \lambda_{\frac{1}{2}n+2} = 0$ for P itself, and $\lambda_{\frac{1}{2}n} = \frac{1}{2}(\sqrt{5} - 1)$ for $\hat{P}$ (= C_{60}).



$$CC^\top = \begin{array}{cc} \begin{array}{cccccc} v_1 & v_2 & v_3 & v_4 & v_5 & v_6 \end{array} & \\ \begin{bmatrix} 3 & 1 & 1 & 1 & \cdot & \cdot \\ 1 & 3 & 1 & \cdot & 1 & \cdot \\ 1 & 1 & 3 & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & 3 & 1 & 1 \\ \cdot & 1 & \cdot & 1 & 3 & 1 \\ \cdot & \cdot & 1 & 1 & 1 & 3 \end{bmatrix} & \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{array} \end{array}$$

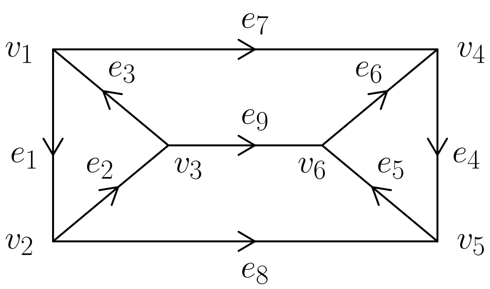
Incidence matrix $C =$

$$\begin{array}{cc} \begin{array}{ccccccccc} e_1 & e_2 & e_3 & e_4 & e_5 & e_6 & e_7 & e_8 & e_9 \end{array} & \\ \begin{bmatrix} 1 & \cdot & 1 & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ 1 & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & 1 & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & 1 & \cdot & 1 & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & 1 & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & 1 & \cdot & \cdot & 1 \end{bmatrix} & \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{array} \end{array}$$

$C^\top C =$

$$\begin{array}{cc} \begin{array}{ccccccccc} e_1 & e_2 & e_3 & e_4 & e_5 & e_6 & e_7 & e_8 & e_9 \end{array} & \\ \begin{bmatrix} 2 & 1 & 1 & \cdot & \cdot & \cdot & 1 & 1 & \cdot \\ 1 & 2 & 1 & \cdot & \cdot & \cdot & \cdot & 1 & 1 \\ 1 & 1 & 2 & \cdot & \cdot & \cdot & 1 & \cdot & 1 \\ \cdot & \cdot & \cdot & 2 & 1 & 1 & 1 & 1 & \cdot \\ \cdot & \cdot & \cdot & 1 & 2 & 1 & \cdot & 1 & 1 \\ \cdot & \cdot & \cdot & 1 & 1 & 2 & 1 & \cdot & 1 \\ 1 & \cdot & 1 & 1 & \cdot & 1 & 2 & \cdot & \cdot \\ 1 & 1 & \cdot & 1 & 1 & \cdot & \cdot & 2 & \cdot \\ \cdot & 1 & 1 & \cdot & 1 & 1 & \cdot & \cdot & 2 \end{bmatrix} & \begin{array}{c} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \\ e_7 \\ e_8 \\ e_9 \end{array} \end{array}$$

All eigenvalues are $\geqslant 0$.



$$\vec{C}\vec{C}^\top = \begin{array}{cc} \begin{array}{cccccc} v_1 & v_2 & v_3 & v_4 & v_5 & v_6 \end{array} & \\ \begin{bmatrix} 3 & -1 & -1 & -1 & \cdot & \cdot \\ -1 & 3 & -1 & \cdot & -1 & \cdot \\ -1 & -1 & 3 & \cdot & \cdot & -1 \\ -1 & \cdot & \cdot & 3 & -1 & -1 \\ \cdot & -1 & \cdot & -1 & 3 & -1 \\ \cdot & \cdot & -1 & -1 & -1 & 3 \end{bmatrix} & \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{array} \end{array}$$

Incidence matrix $\vec{C} =$

$$\begin{array}{cc} \begin{array}{ccccccccc} e_1 & e_2 & e_3 & e_4 & e_5 & e_6 & e_7 & e_8 & e_9 \end{array} & \\ \begin{bmatrix} -1 & \cdot & 1 & \cdot & \cdot & \cdot & -1 & \cdot & \cdot \\ 1 & -1 & \cdot & \cdot & \cdot & \cdot & \cdot & -1 & \cdot \\ \cdot & 1 & -1 & \cdot & \cdot & \cdot & \cdot & \cdot & -1 \\ \cdot & \cdot & \cdot & -1 & \cdot & 1 & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & -1 & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & -1 & \cdot & \cdot & 1 \end{bmatrix} & \begin{array}{c} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{array} \end{array}$$

$\vec{C}^\top \vec{C} =$

$$\begin{array}{cc} \begin{array}{ccccccccc} e_1 & e_2 & e_3 & e_4 & e_5 & e_6 & e_7 & e_8 & e_9 \end{array} & \\ \begin{bmatrix} 2 & -1 & -1 & \cdot & \cdot & \cdot & 1 & -1 & \cdot \\ -1 & 2 & -1 & \cdot & \cdot & \cdot & \cdot & 1 & -1 \\ -1 & -1 & 2 & \cdot & \cdot & \cdot & -1 & \cdot & 1 \\ \cdot & \cdot & \cdot & 2 & -1 & -1 & -1 & 1 & \cdot \\ \cdot & \cdot & \cdot & -1 & 2 & -1 & \cdot & -1 & 1 \\ \cdot & \cdot & \cdot & -1 & -1 & 2 & 1 & \cdot & -1 \\ 1 & \cdot & -1 & -1 & \cdot & 1 & 2 & \cdot & \cdot \\ -1 & 1 & \cdot & 1 & -1 & \cdot & \cdot & 2 & \cdot \\ \cdot & -1 & 1 & \cdot & 1 & -1 & \cdot & \cdot & 2 \end{bmatrix} & \begin{array}{c} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \\ e_7 \\ e_8 \\ e_9 \end{array} \end{array}$$

All eigenvalues are $\geqslant 0$.