3.012 Fund of Mat Sci: Bonding – Lecture 13

THE DANCE OF SHIVA

Source: Wikipedia

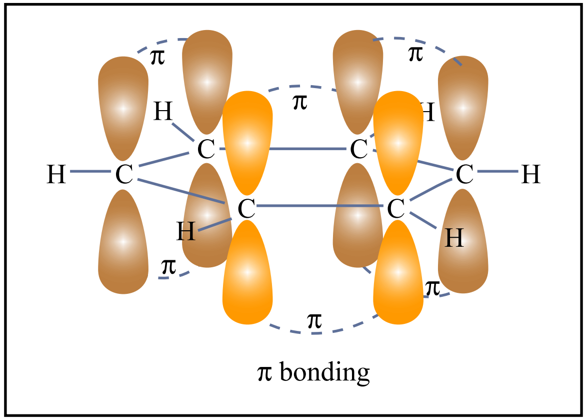
Homework for Mon Oct 31

- Study:18.1 (quantum oscillator), 28.1 and 28.2 (symmetry)
- Read 18.6 (classical harmonic oscillator)

Last time:

1. Diagonalization in a basis
2. Huckel model for conjugated and aromatic polymers

$$|\psi\rangle = \sum_{n=1,k} c_n |\varphi_n\rangle$$



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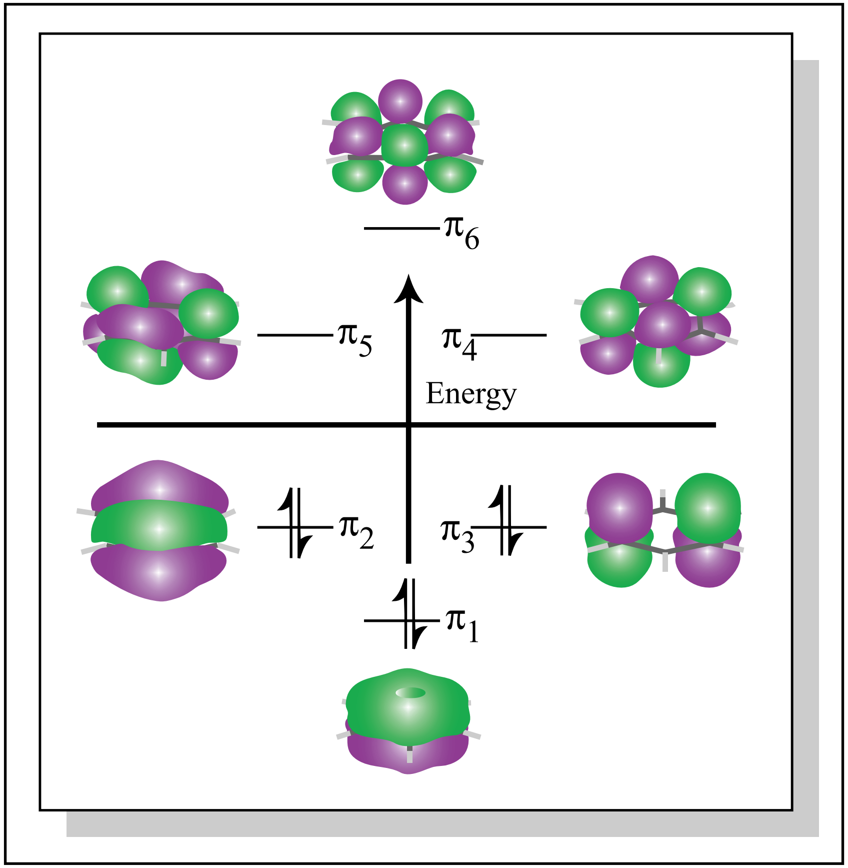

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Matrix Formulation

$$|\psi\rangle = \sum_{n=1,k} c_n |\varphi_n\rangle \qquad H_{mn} = \langle \varphi_m | \hat{H} | \varphi_n \rangle$$

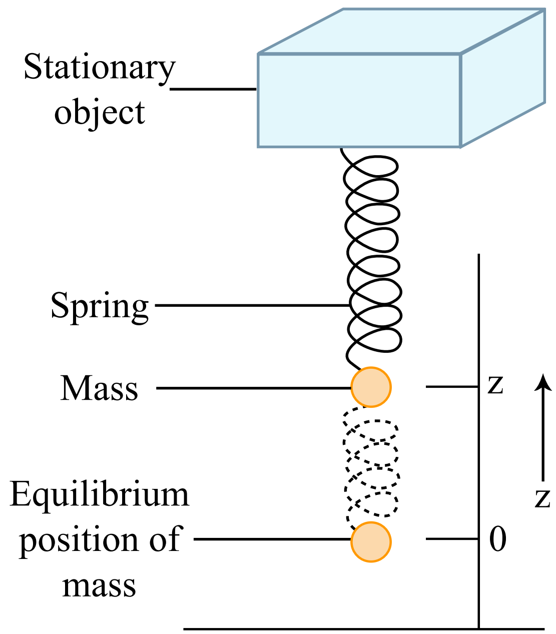
$$\begin{pmatrix} H_{11} - E & \ldots\ldots & & H_{1k} \\ . & H_{22} - E & & \\ . & & & . \\ . & & \ddots & . \\ H_{k1} & \ldots\ldots & & H_{kk} - E \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ . \\ . \\ . \\ c_k \end{pmatrix} = 0$$

The Quantization of Vibrations

- Electrons are much lighter than nuclei ($m_{proton}/m_{electron} \sim 1800$)
- Electronic wave-functions always rearrange themselves to be in the ground state (lowest energy possible for the electrons), even if the ions are moving around
- Born-Oppenheimer approximation: electrons in the instantaneous potential of the ions (so, electrons can not be excited – FALSE in general)

Nuclei have some quantum action…

- Go back to Lecture 1 – remember the harmonic oscillator



A mass on a spring. This system can be represented by a harmonic oscillator.

Graph of Potential energy, V(x), as a function of the bond length, x, for a diatomic molecule.

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See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 378, figure 18.1.

Figure by MIT OCW.

The quantum harmonic oscillator

$$-\frac{\hbar^2}{2M}\frac{d^2\varphi(z)}{dz^2}+\frac{1}{2}kz^2\varphi(z)=E\varphi(z)$$

$$\omega=\sqrt{\frac{k}{m}} \qquad a=\frac{\sqrt{km}}{\hbar}$$

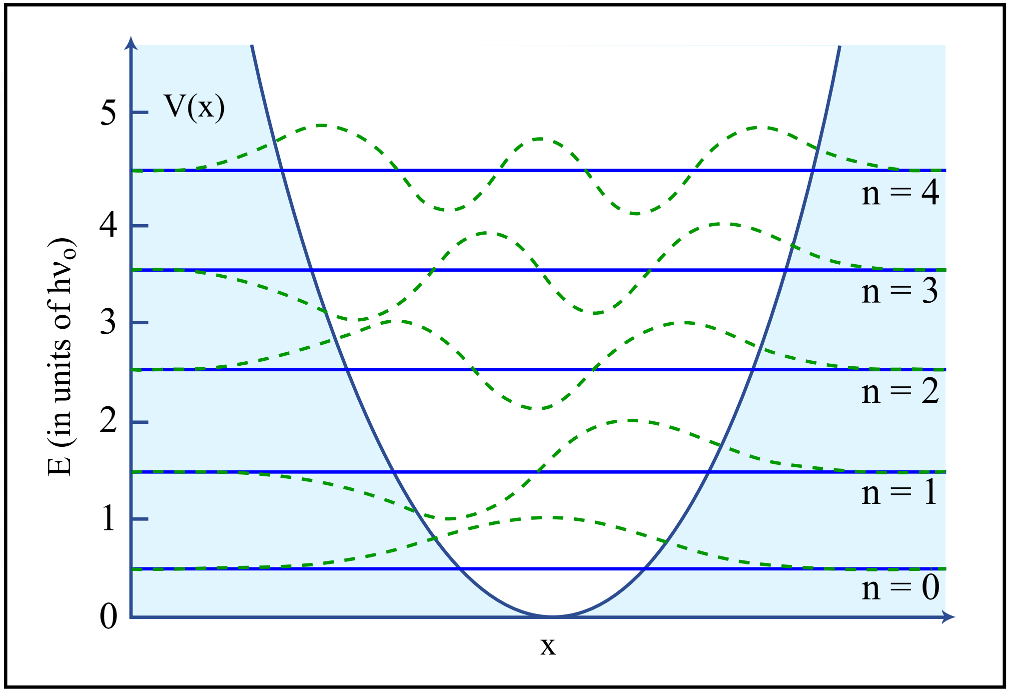
The quantum harmonic oscillator (II)

$$\psi_0 = \left(\frac{a}{\pi}\right)^{1/4} e^{-az^2/2}$$

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} z e^{-az^2/2}$$

$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2az^2 - 1) e^{-az^2/2}$$

$$E = \hbar\omega\left(n + \frac{1}{2}\right)$$



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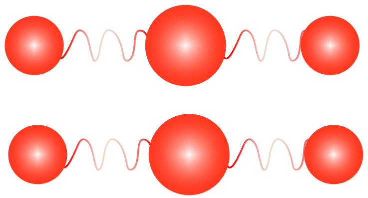
Quantum Oscillator Applet

Quantized atomic vibrations



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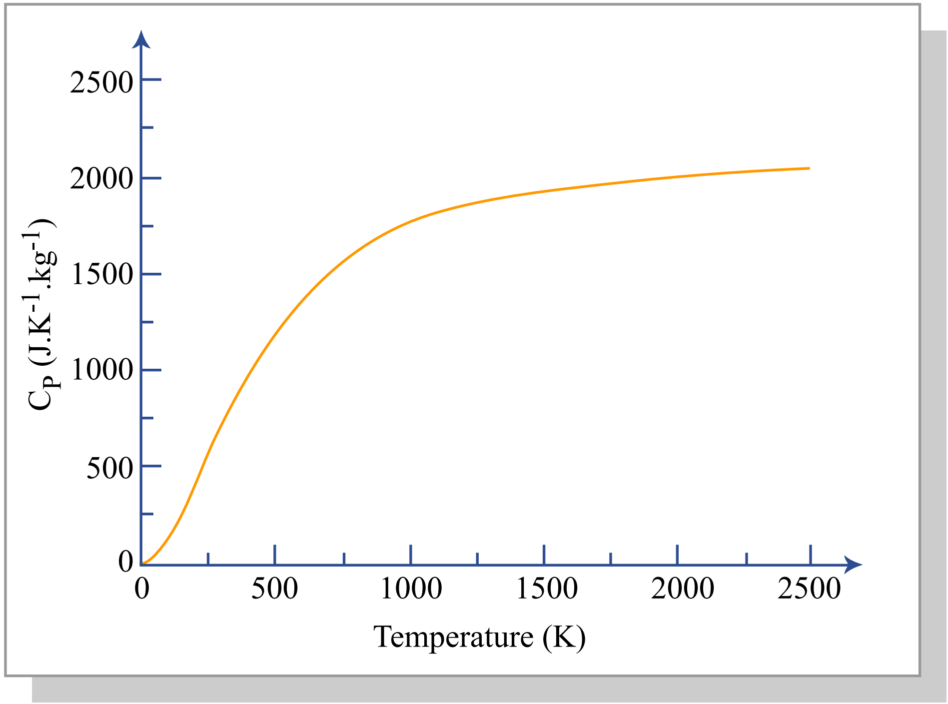
See http://w3.rz-berlin.mpg.de/%7Ehermann/hermann/Phono1.gif.

Photo courtesy of Malene Thyssen, www.mtfoto.dk/malene/

Specific Heat of Graphite (Dulong and Petit)



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Structure

Symmetry

- Symmetry operations: actions that transform an object into a new but undistinguishable configuration
- Symmetry elements: geometric entities (axes, planes, points…) around which we carry out the symmetry operations

Figure 17.1b

Images of the symmetry elements of the allene (CH_2CCH_2) and PCl_5 molecules removed for copyright reasons.

See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 658, figure 28.1.

Table 28.1

Table of symmetry elements and their corresponding operations removed for copyright reasons.

See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 658, table 28.1.

Group Therapy…

A group G is a finite or infinite set of elements A, B, C, D…together with an operation "☼" that satisfy the four properties of:

1. Closure: If A and B are two elements in G, then A☼B is also in G.
2. Associativity: For all elements in G, (A☼B) ☼C==A☼ (B☼C).
3. Identity: There is an identity element I such that I☼A=A☼I=A for every element A in G.
4. Inverse: There is an inverse or reciprocal of each element. Therefore, the set must contain an element B=inv(A) such that A☼inv(A)=inv(A) ☼A=I for each element of G.

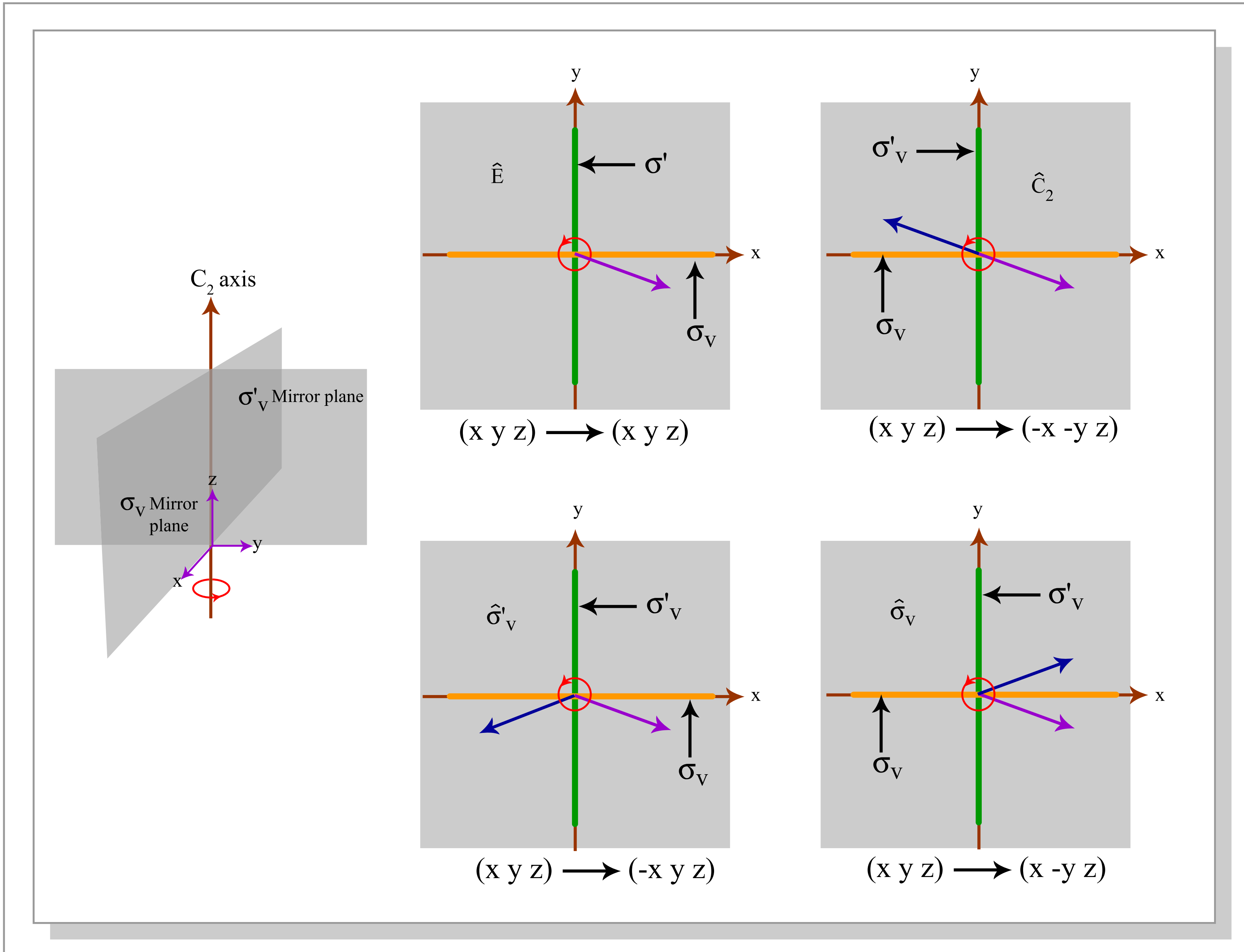
Examples

- Integer numbers, and addition
- Integer numbers, and multiplication
- Real numbers, and multiplication
- Rotations around an axis by 360/n

Figure 17.3

Image of mirror planes in a water molecule removed for copyright reasons.

See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 663, figure 28.3.



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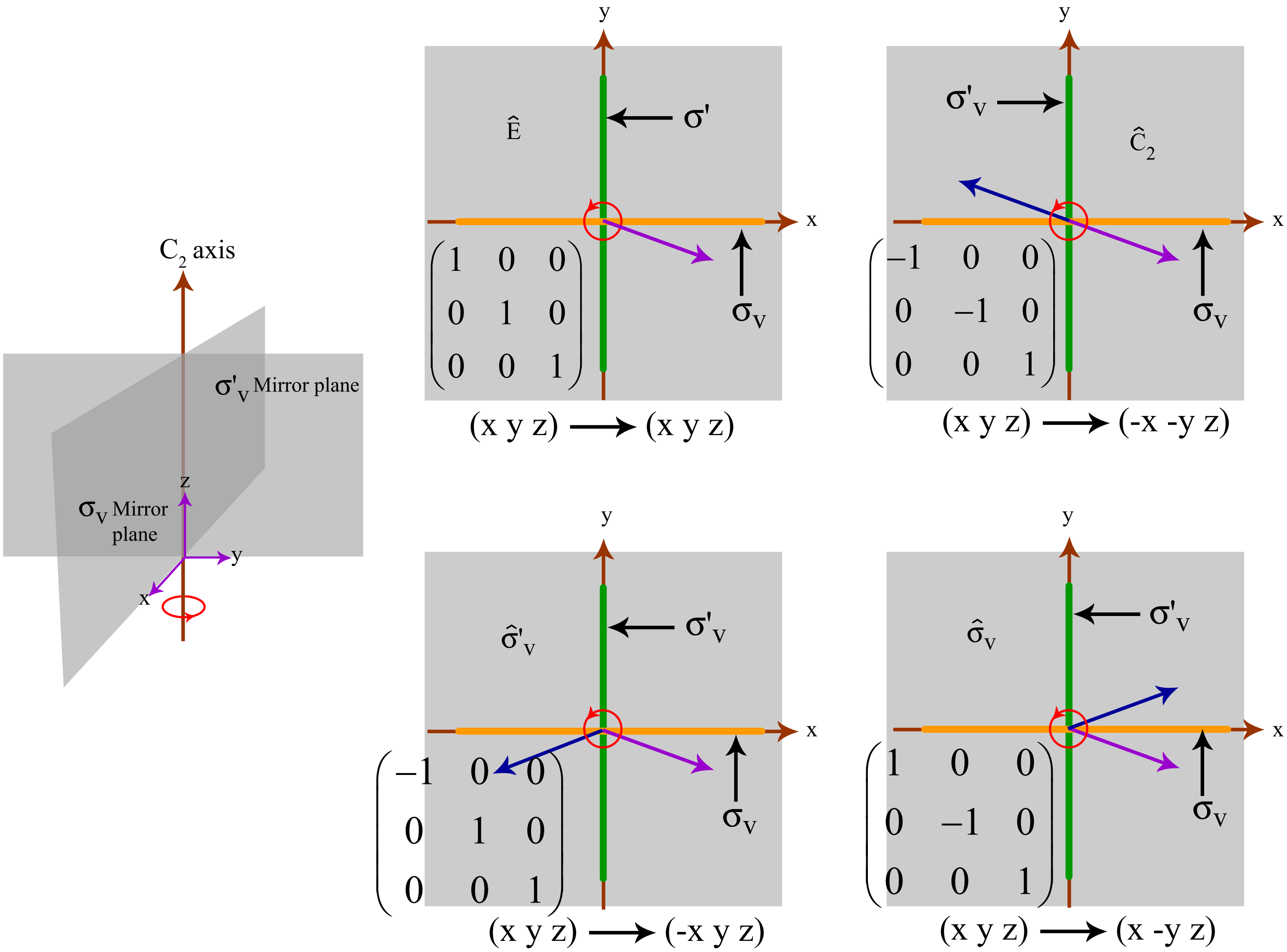

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Figure by MIT OCW.

Table 17.3

Multiplication Table for Operators of the C_{2V} Group removed for copyright reasons.

See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 666, table 28.3.

D_{2h} (dihedral)

Image of the Symmetry elements of the D_{2h} group in ethene removed for copyright reasons.

See Engel, T., and P. Reid. *Physical Chemistry*. Single volume ed. San Francisco, CA: Benjamin Cummings, 2005, p. 682, figure 28.10.