3.012 Fund of Mat Sci: Bonding – Lecture 12

POLYMERSPOLYMERSPOLYMERSPOLYMERSPOLYMERSPOLYMERSPOLYMERS

Image of a DNA strand removed for copyright reasons.

Homework for Fri Oct 21

- Study:25.7 (Huckel model), 18.1 (quantum oscillator),
- Read 18.6 (classical harmonic oscillator)

Last time:

1. Hartree and Hartree-Fock equations
2. Slater determinants
3. H_2 solution
4. Symmetries
5. Homonuclear diatomic levels
6. Bond order

Fluorine dimer F_2

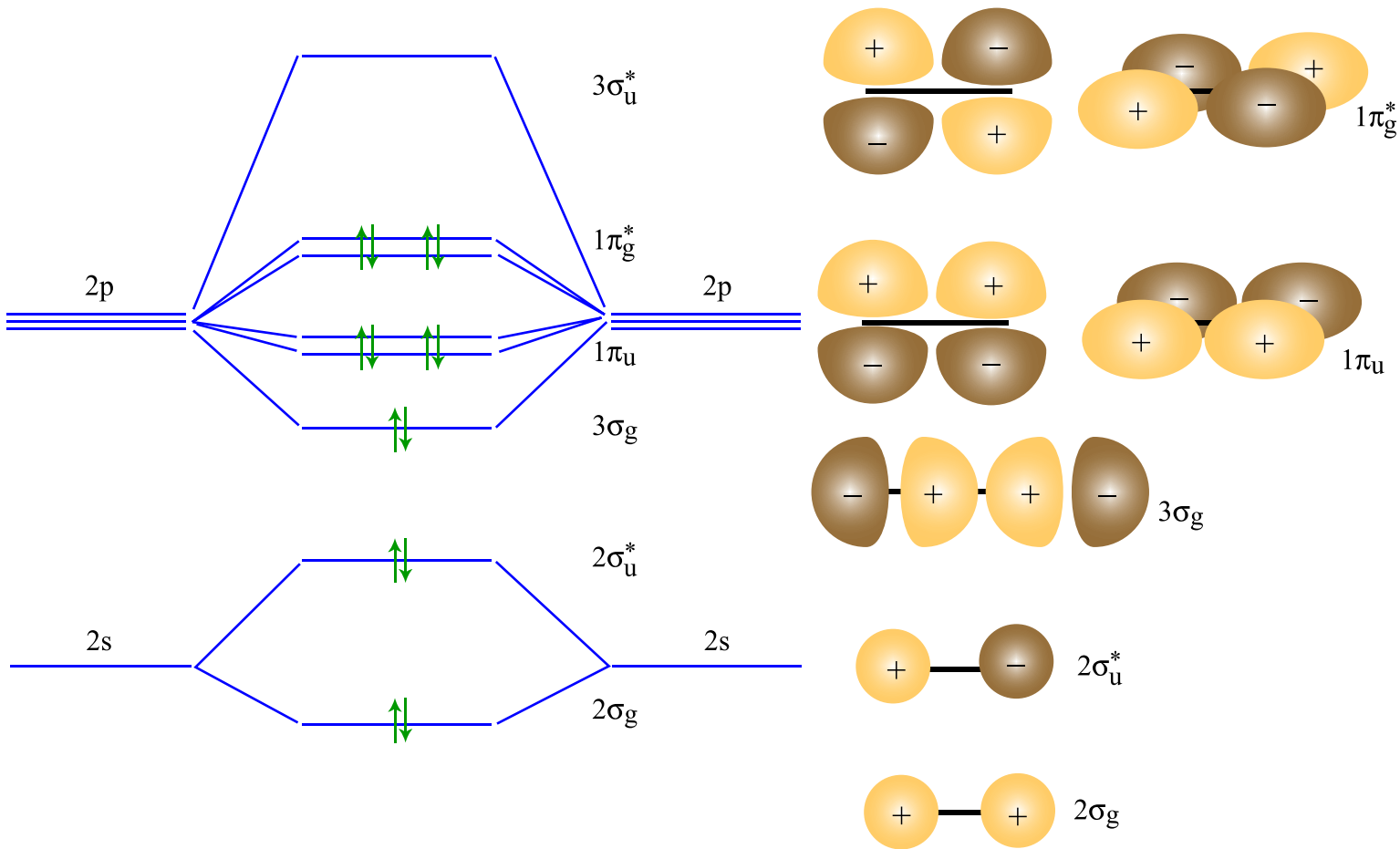


Figure by MIT OCW.

Correction: Nodal plane containing molecular axis → π

Matrix Formulation (I)

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

$$\left|\psi\right\rangle = \sum_{n=1,k} c_n \left|\varphi_n\right\rangle \qquad \left\{\left|\varphi_n\right\rangle\right\} \text{ orthogonal}$$

$$\left\langle\varphi_m\right|\hat{H}\left|\psi\right\rangle = E\left\langle\varphi_m\right|\left.\psi\right\rangle$$

$$\sum_{n=1,k} c_n \left\langle\varphi_m\right|\hat{H}\left|\varphi_n\right\rangle = Ec_m$$

Matrix Formulation (II)

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix} H_{11} & \cdots\cdots & H_{1k} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ H_{k1} & \cdots\cdots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix}$$

Matrix Formulation (III)

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

Empirical tight binding and Hückel approach

- TB: The matrix elements of the Hamiltonian are "universal empirical parameters"
- Hückel: Planar / quasi-planar systems with delocalized π bonding: two parameters
  - α: matrix element between same orbital
  - β: matrix element between neighboring orbitals
  - Hamiltonian between further neighbors is 0

Example: Benzene (C_6H_6)

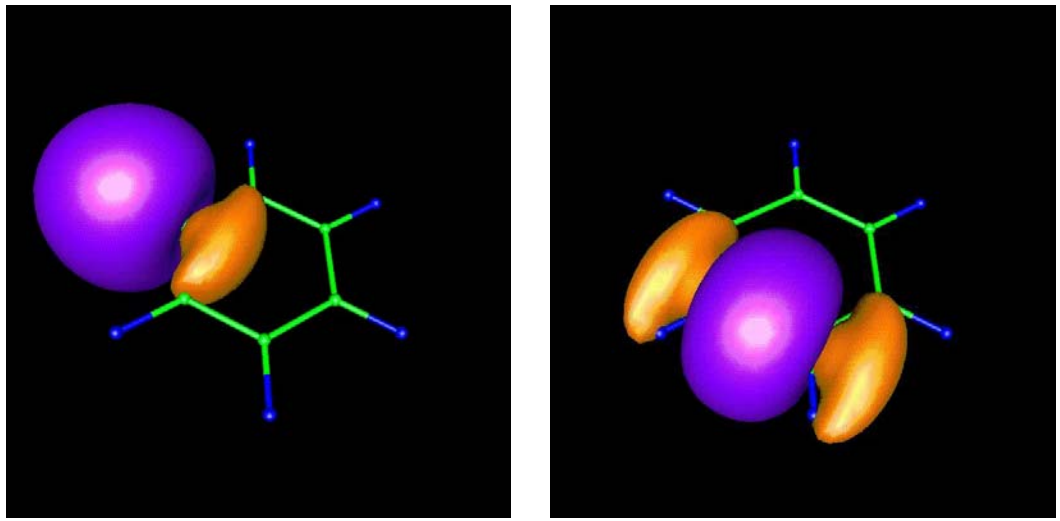


Diagram of the sigma bond network of benzene removed for copyright reasons.

See page 462, Figure 12-26 in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.

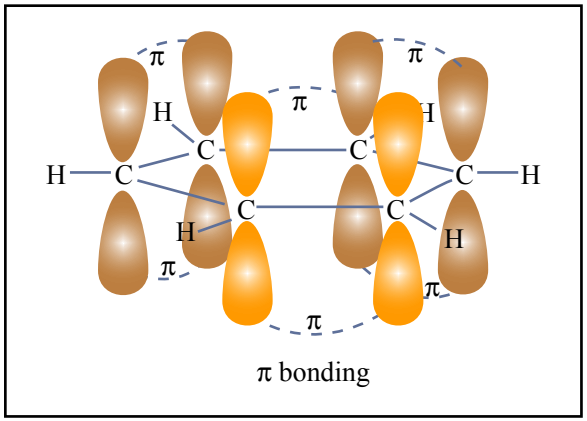


Figure by MIT OCW.

Benzene – energy levels

$$\det\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix} = 0$$

Benzene – molecular orbitals

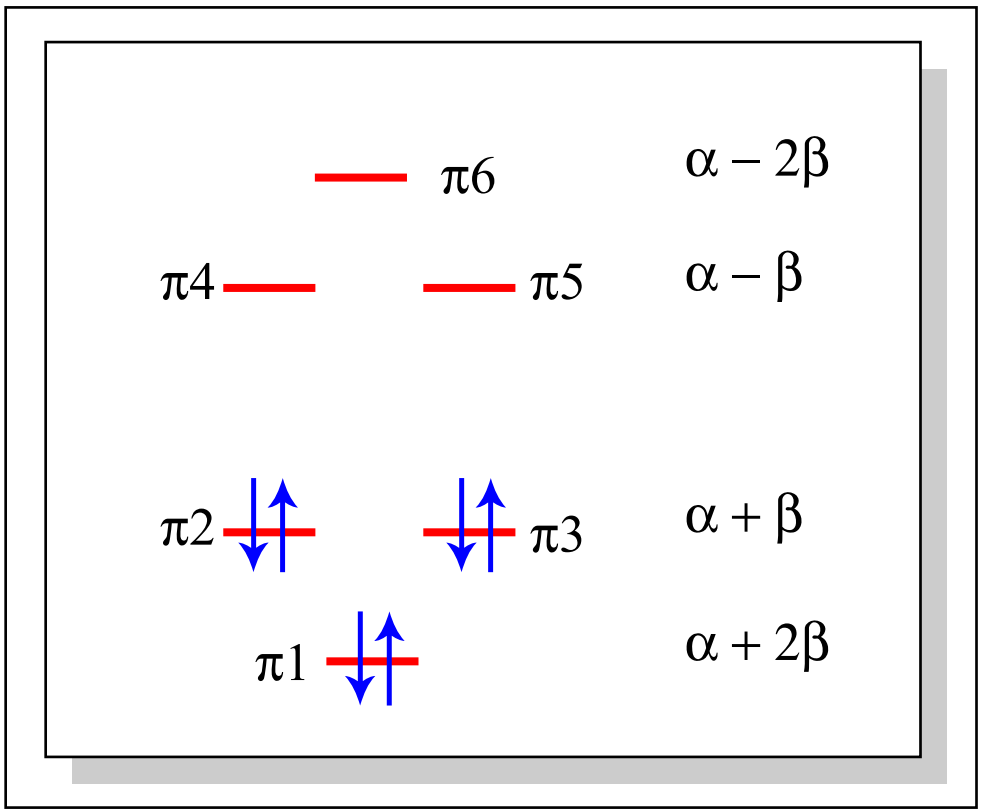


Figure by MIT OCW.

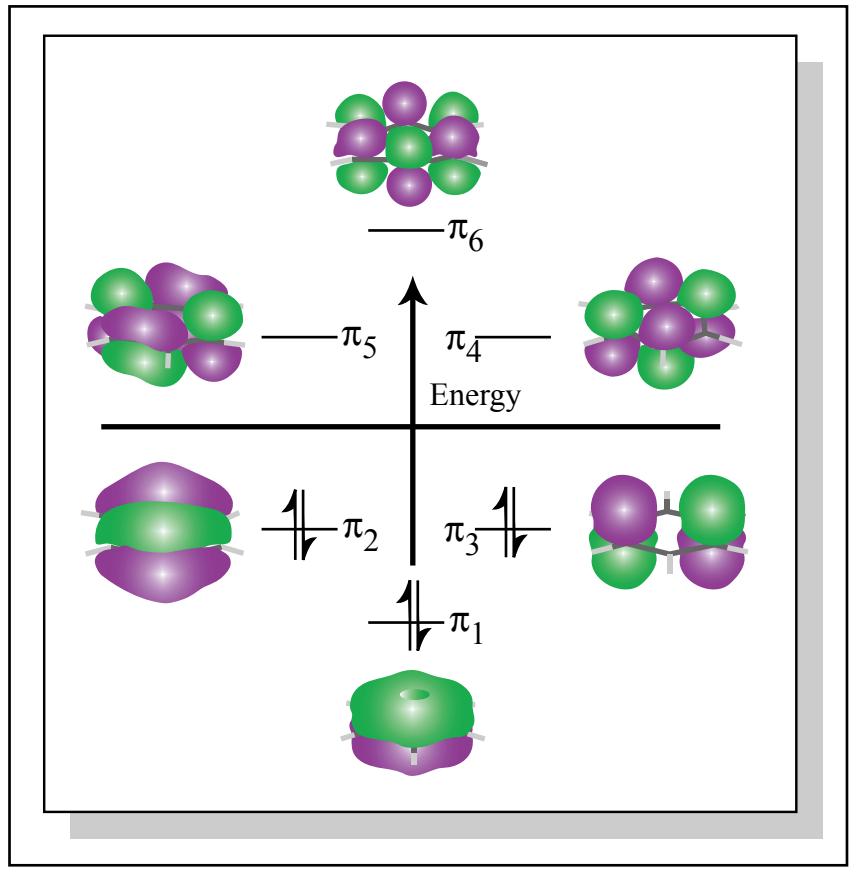


Figure by MIT OCW.

HOMO-LUMO in naphthalene

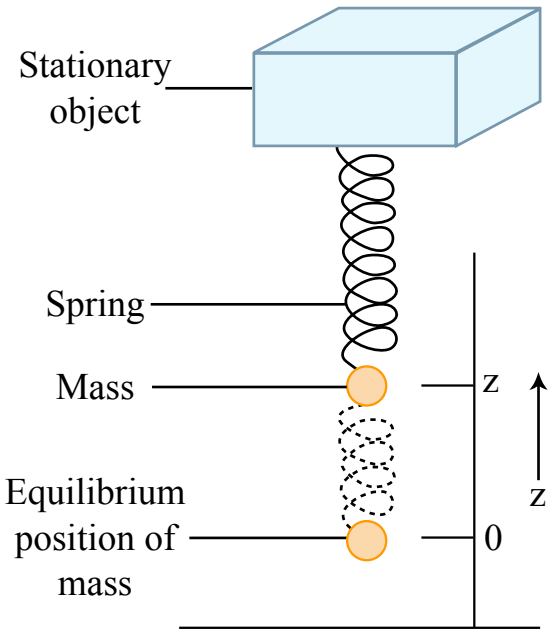
Images of orbitals in naphthalene removed for copyright reasons.

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)

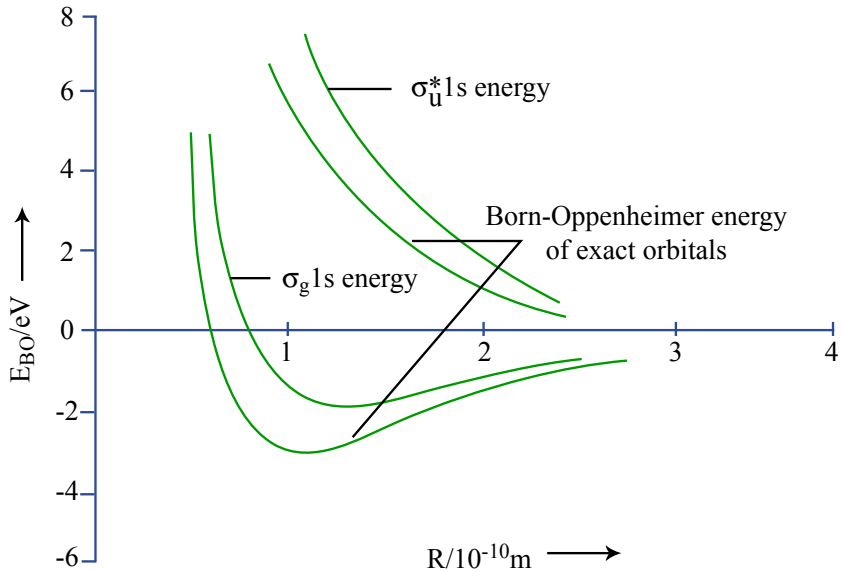
Nuclei have some quantum action…

- Go back to Lecture 1 – remember the harmonic oscillator



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

Figure by MIT OCW.

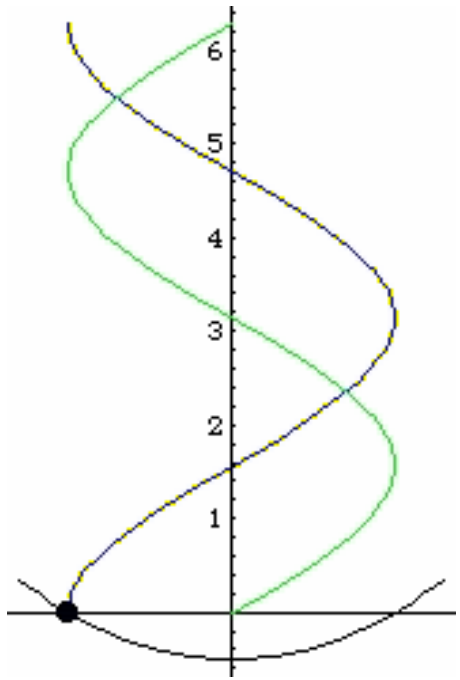


Orbital Energies for the σ_g 1s and σ_u^* 1s LCAO Molecular Orbitals.

Figure by MIT OCW.

The quantum harmonic oscillator (I)

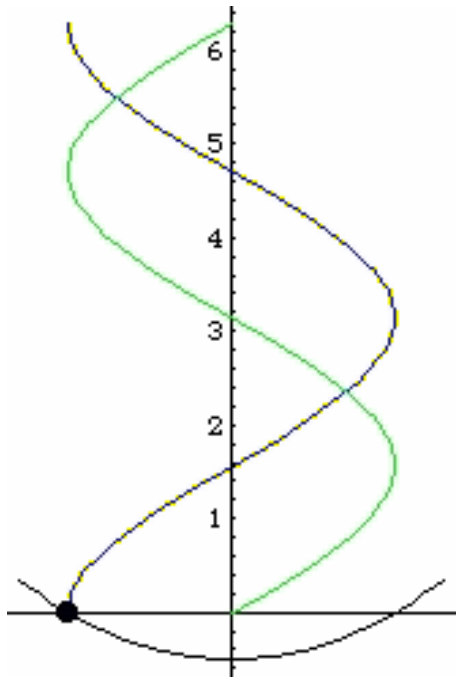
$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + \frac{1}{2}kz^2 \right)\varphi(z) = E\,\varphi(z)$$



The quantum harmonic oscillator (I)

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

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



The quantum harmonic oscillator (II)

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

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

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

Graph of harmonic oscillator wave functions removed for copyright reasons.

See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 532, figure 14.21.

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

Quantized atomic vibrations

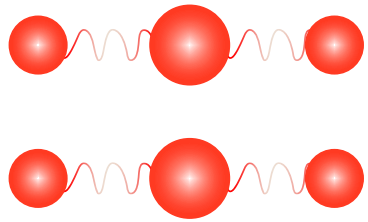


Figure by MIT OCW.

Image removed for copyright reasons.
See http://w3.rz-berlin.mpg.de/%7Ehermann/hermann/Phono1.gif.

Specific Heat of Graphite (Dulong and Petit)

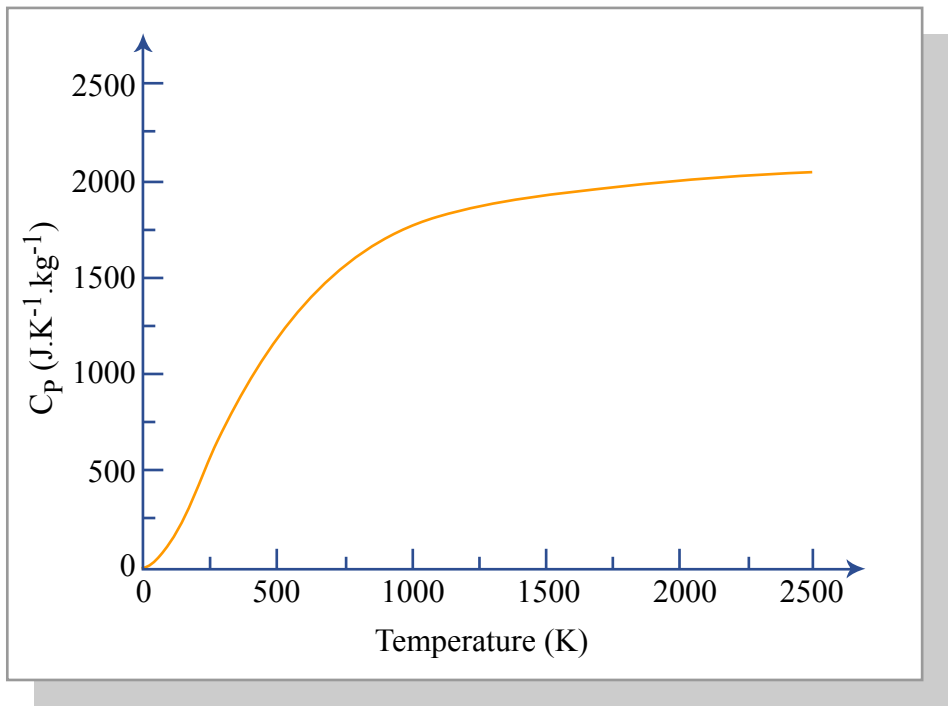


Figure by MIT OCW.