3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

3.23 Fall 2007 – Lecture 6

VARIATIONS AND VIBRATIONS

Last time

1. Orbitals in atoms, nodal surfaces
2. Good quantum numbers
3. Spin
4. Spin-statistics, Pauli principle, auf-bau filling of the periodic table
5. Mean field solutions for non-hydrogenoid atoms in a central potential

Study

- “Study 4” posted: Prof Fink’s notes on lattice dynamics

From waves to vector space

A vector space *V* is a set which is closed under "vector addition" and "scalar multiplication"
We start with an abelian group, with an operation "+" and elements "u, v,…"

1. Commutative: $u+v=v+u$
2. Associative: $(u+v)+w=u+(v+w)$
3. Existence of zero: $0+u=u+0=u$
4. Existence of inverse –u: $u+(-u)=0$

We add a scalar multiplication by "α,β…"

5. Associativity of scalar multiplication: $\alpha(\beta u)= (\alpha\beta)u$
6. Distributivity of scalar sums: $(\alpha+\beta)u=\alpha u+\beta u$
7. Distributivity of vector sums: $\alpha(u+v)= \alpha u+ \alpha v$
8. Scalar multiplication identity: $1u=u$

Dirac's <bra|kets> (elements of vector space)

$$\psi = \psi(\vec{r}) = \left|\psi\right\rangle$$

Scalar product induces a metric → Hilbert space

$$\int \psi_i^*(\vec{r})\psi_j(\vec{r})\,d\vec{r} = \left\langle \psi_i \middle| \psi_j \right\rangle \quad \left(= \delta_{ij} \text{ if orthogonal}\right)$$

Expectation values

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

$$\left\langle\psi\right|\hat{H}\left|\psi\right\rangle$$

Matrix Formulation (I)

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

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

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

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

Matrix Formulation (II)

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

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

Matrix Formulation (III)

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

Variational Principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E[\Psi] \geq E_0$$

If $E[\Psi] = E_0$, then Φ is the ground state wavefunction, and viceversa…

Atomic Units

- m_e=1, e=1, a_0 (Bohr radius)=1, $\hbar = 1$

$$\varepsilon_0 = \frac{1}{4\pi}$$

Energy of 1s electron$= -\frac{1}{2}\frac{Z^2}{n^2}$

(1 atomic unit of energy=1 Hartree=2 Rydberg=27.21 eV

Energy of an Hydrogen Atom

$$E_\alpha = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle}$$

$$\Psi_\alpha = C \exp(-\alpha r)$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = \pi \frac{C^2}{\alpha^3}, \qquad \langle \Psi_\alpha | -\frac{1}{2}\nabla^2 | \Psi_\alpha \rangle = \pi \frac{C^2}{2\alpha} \qquad \langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -\pi \frac{C^2}{\alpha^2}$$

Hydrogen Molecular Ion H_2^+

- Born-Oppenheimer approximation: the electron is always in the ground state corresponding to the instantaneous ionic positions

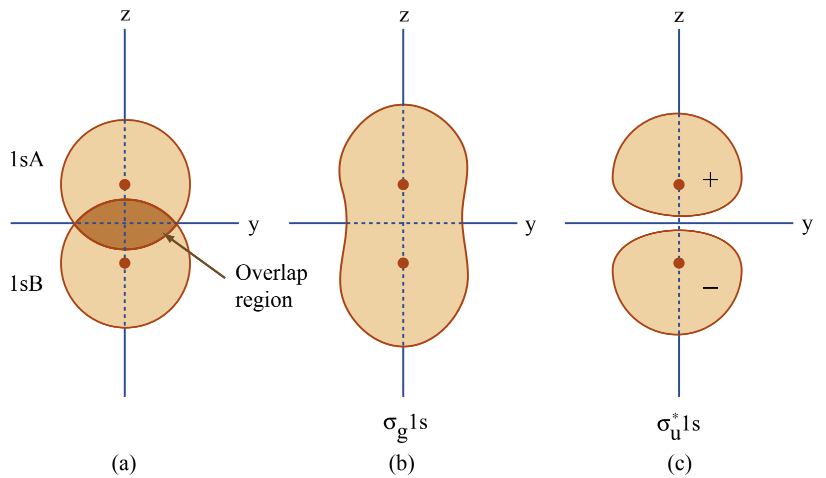
$$\left[-\frac{1}{2}\nabla^2+\left(\frac{1}{\left|\vec{R}_{H_1}-\vec{R}_{H_2}\right|}-\frac{1}{\left|r-\vec{R}_{H_1}\right|}-\frac{1}{\left|r-\vec{R}_{H_2}\right|}\right)\right]\psi(\vec{r})=E\psi(\vec{r})$$

Linear Combination of Atomic Orbitals

- Most common approach to find out the ground-state solution – it allows a meaningful definition of “hybridization”, “bonding” and “anti-bonding” orbitals.
- Also knows as LCAO, LCAO-MO (for molecular orbitals), or tight-binding (for solids)
- Trial wavefunction is a linear combination of atomic orbitals – the variational parameters are the coefficients:

$$\Psi_{trial} = c_1 \Psi_{1s}\left(\vec{r} - \vec{R}_{H_1}\right) + c_2 \Psi_{1s}\left(\vec{r} - \vec{R}_{H_2}\right)$$

Bonding and Antibonding (I)



The orbital region for the σ_g1s and σ 1s LCAO molecular orbitals. (a) The overlapping orbital regions of the 1sA and 1sB atomic orbitals. (b) The orbital region of the σ_g1s LCAO-MO. (c) The orbital Region of the σ 1s LCAO-MO. The orbital regions of the LCAO molecular orbitals have the same general features as the "exact" Born Oppenheimer orbitals whose orbital regions were depicted in Figure 18.4.

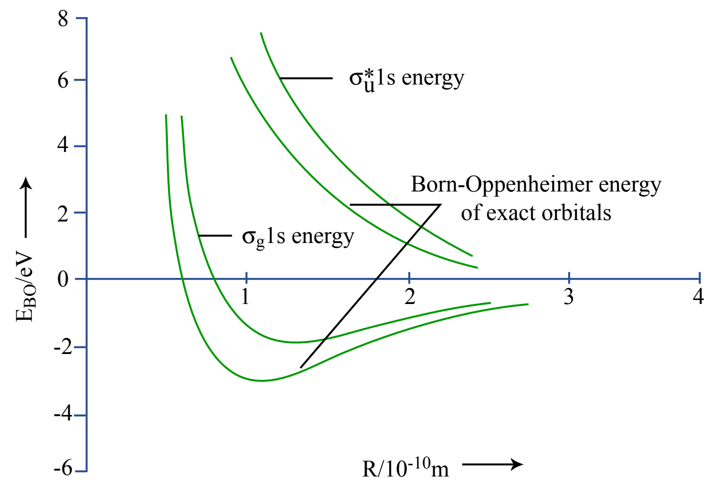
Figure by MIT OpenCourseWare.

Formation of a Bonding Orbital

Image removed due to copyright restrictions. Please see
the animation of hydrogen bonding orbitals at http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma/index.html

Formation of an Antibonding Orbital

Bonding and Antibonding (II)



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

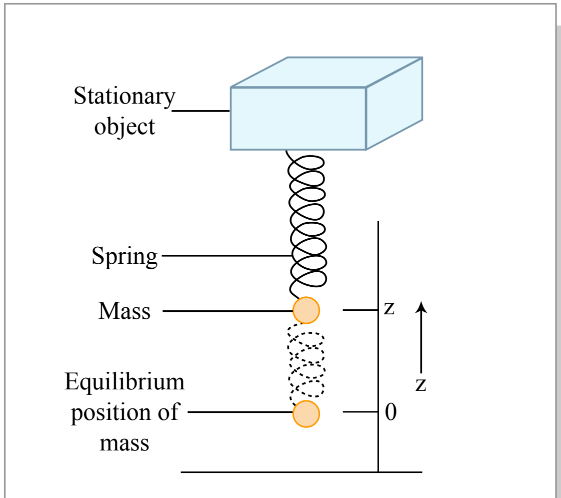
Figure by MIT OpenCourseWare.

The Quantization of Vibrations

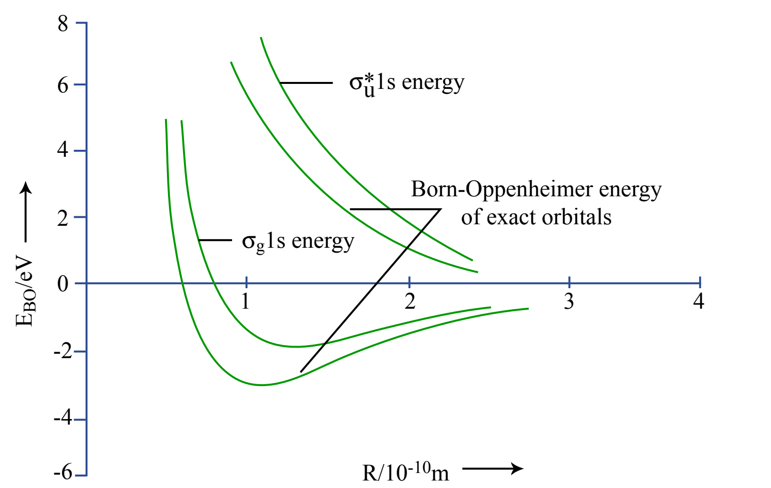
- Electrons are much lighter than nuclei ($m_{proton}/m_{electron}$~1800)
- Electronic wave-functions always rearrange themselves to be in the ground state (lowest energy possible for the electrons), even if the ions are moving around
- Born-Oppenheimer approximation: electrons in the instantaneous potential 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.

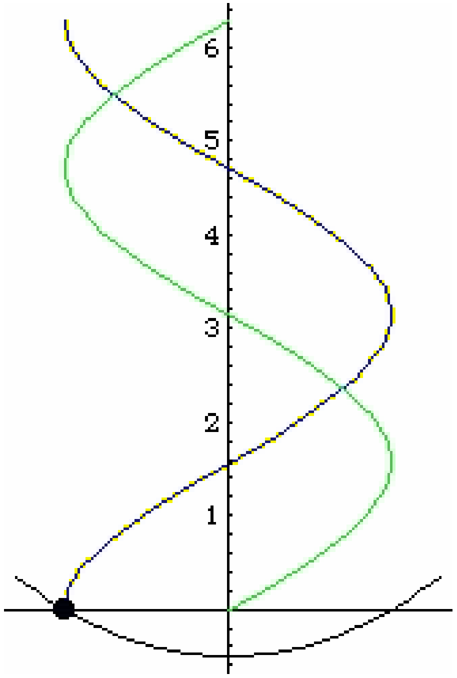


Orbital Energies for the σ_g 1s and σ_u^* 1s LCAO Molecular Orbitals.

Figures by MIT OpenCourseWare.

The quantum harmonic oscillator (I)

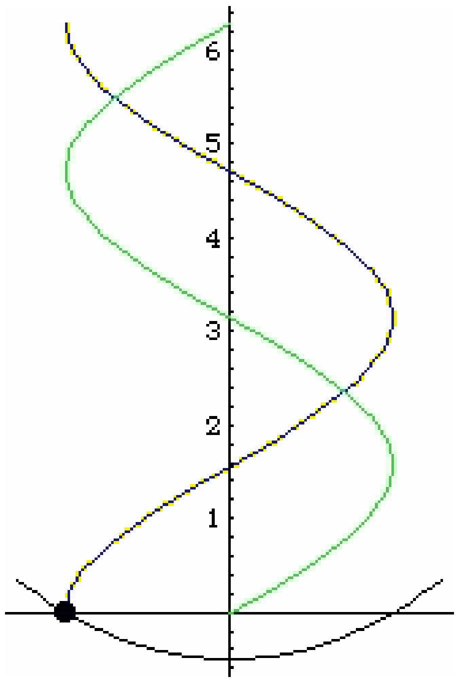
$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + \frac{1}{2}kz^2 \right)\varphi(z) = E\,\varphi(z)$$



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)

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

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

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

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

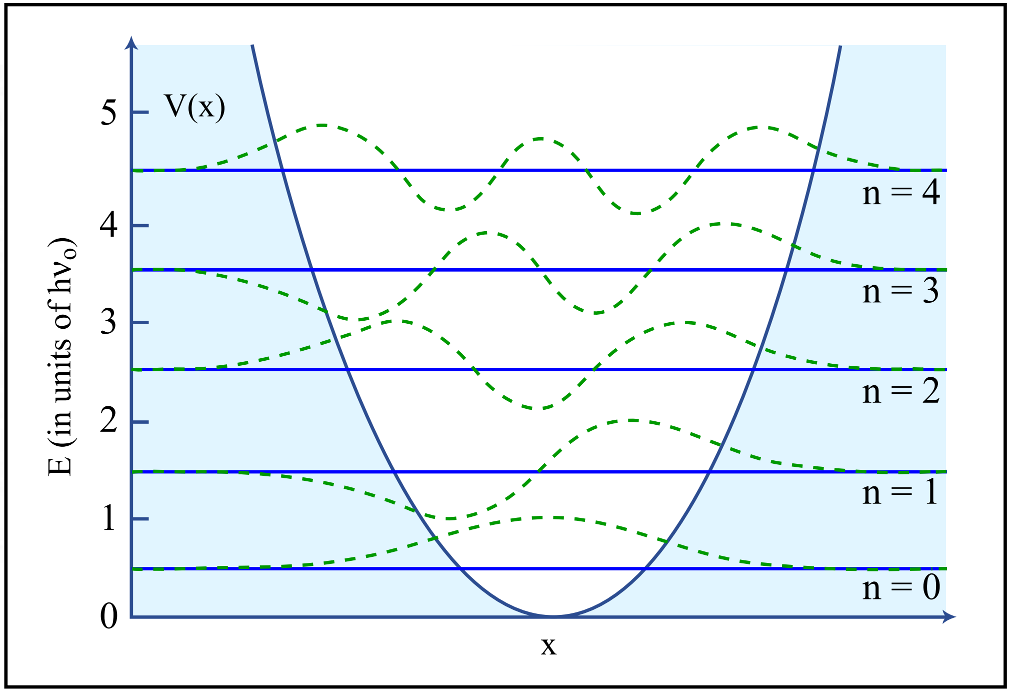
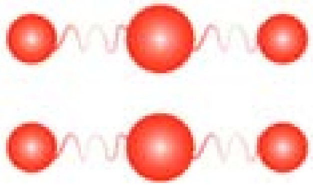


Figure by MIT OpenCourseWare.

Quantized atomic vibrations



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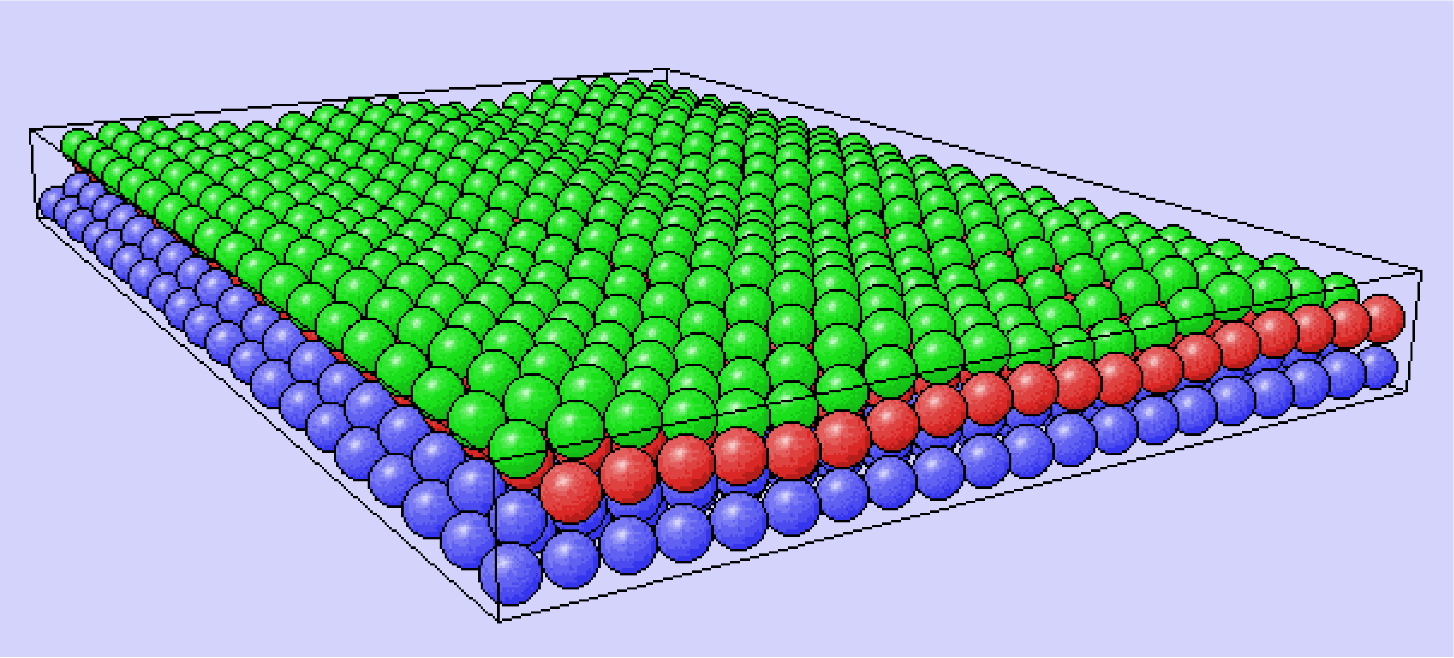
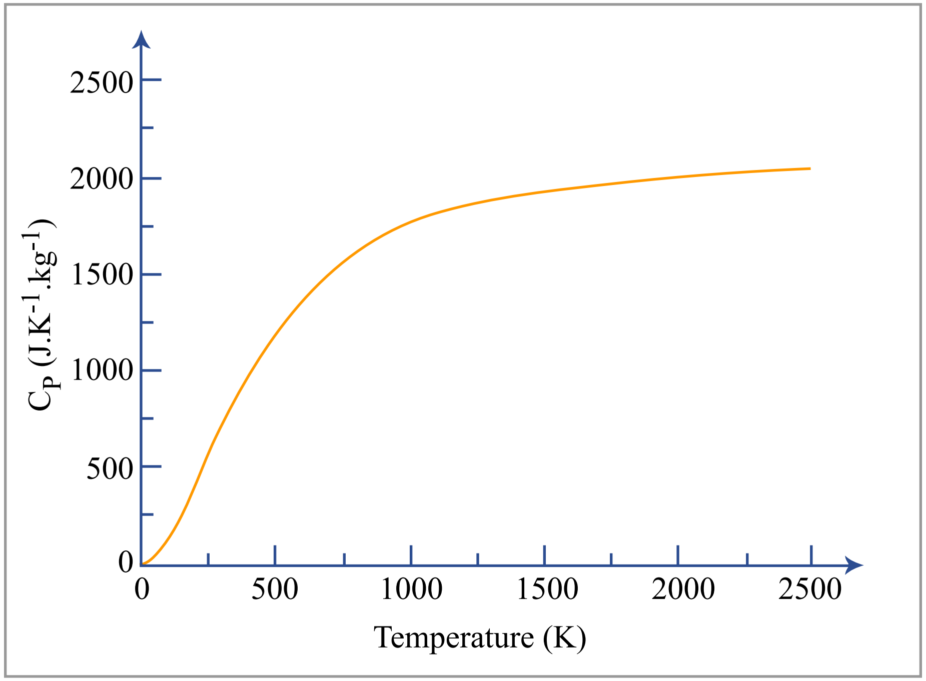


Courtesy of Dr. Klaus Hermann. Used with permission.

Specific Heat of Graphite (Dulong and Petit)



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