

3.012 Fund of Mat Sci: Bonding – Lecture 9

VARIATIONS

Homework for Fri Oct 14

- Study: 21.4, 23.3
- Read: 23.4, 24.1, 24.2

Last time:

1. Screening, and coupled, self-consistent Hartree equations for many-electron atoms
2. 4th quantum number: spin
3. Filling (auf-bau) of the periodic table
4. Physical trends on sizes, IP, EA. (e.g., why He is smaller than H)

Variational Principle

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

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

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

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

Good Quantum Numbers

$$\frac{d \langle \hat{A} \rangle}{dt} = \frac{d \langle \Psi | \hat{A} | \Psi \rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle$$

If \hat{A} commutes with the Hamiltonian, its expectation value does not change with time (it's a constant of motion – if we are in an eigenstate, that quantum number will remain constant)

Atomic Units

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

$$\epsilon_0 = \frac{1}{4\pi}$$

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

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

Energy of an Hydrogen Atom

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

Energy of an Hydrogen Atom

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

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

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

Hydrogen Molecular Ion H_2^+

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

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 known 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:

$$\Psi_{trial} = c_1 \Psi_{1s}(\vec{r} - \vec{R}_A) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_B)$$

Linear Combination of Atomic Orbitals

$$\Psi_{trial} = c_1 \Psi_{1s}(\vec{r} - \vec{R}_A) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_B)$$

Bonding and Antibonding (I)

Image of the orbital region for LCAO molecular orbitals removed for copyright reasons.
See Mortimer, R. G. *Physical Chemistry*. 2nd ed. San Diego, CA: Elsevier, 2000, p. 657, figure 18.7.

Hydrogen Molecular Ion H_2^+

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