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

$$E[\Psi] \ge E_0$$

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

Good Quantum Numbers

$$\frac{d\langle \hat{A} \rangle}{dt} = \frac{d\langle \Psi | \hat{A} | \Psi \rangle}{dt} = \frac{1}{ih} \langle \left[\hat{A}, \hat{H} \right] \rangle$$

If 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, $\hbar=1$

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

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

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

Energy of an Hydrogen Atom

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

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

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

Hydrogen Molecular Ion H₂⁺

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

Linear Combination of Atomic Orbitals

- Most common approach to find out the groundstate 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:

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

Linear Combination of Atomic Orbitals

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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 H₂⁺

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