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

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

$$\langle \psi | \psi \rangle = \int_V \psi^*(\vec{r})\, \psi(\vec{r})\, d\vec{r}$$

$$\langle \psi H | \psi \rangle = \int_V \psi^*(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(r)\psi(r) \right]$$

Variational Principle

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

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

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \underline{\underline{V(\vec{r})}}$$

$$\hat{H}\,|\varphi_i\rangle = \varepsilon_i \underbrace{|\varphi_i\rangle}_{\text{COMPLETE SET OF EIGENFUNCTIONS}}$$

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

$$= \sum_i c_i\,\varphi_i(\vec{r})$$

$$\langle \psi | \psi \rangle = \int \left(\sum_i c_i \varphi_i(\vec{r}) \right)^* \left(\sum_j c_j \varphi_j(\vec{r}) \right) =$$

$$= \sum_{i,j} c_i^* c_j \int \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) =$$

$$= \sum_{i,j} c_i^* c_j \underbrace{\langle \varphi_i | \varphi_j \rangle}_{= \delta_{i,j}} = \sum_i c_i^* c_i = \sum_i \| c_i \|^2$$

$$\langle \psi | H | \psi \rangle = \sum_i c_i^* \langle \varphi_i | \, | H | \sum_j c_j | \varphi_j \rangle =$$

$$[H | \varphi_j \rangle = \varepsilon_j | \varphi_j \rangle]$$

$$= \sum_{i,j} c_i^* c_j \langle \varphi_i | \varepsilon_j | \varphi_j \rangle =$$

$$= \sum_{i,j} c_i^* c_j \varepsilon_j \langle \varphi_i | \varphi_j \rangle = \sum_i \| c_i \|^2 \varepsilon_i \geq \sum_i \| c_i \|^2 \varepsilon_0$$

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

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

$-\frac{\hbar^2}{2m} \mapsto -\frac{1}{2}$

$V(r) \to -\frac{1}{r}$

Energy of an Hydrogen Atom

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

$\Rightarrow \psi = Ce^{-\alpha r}$

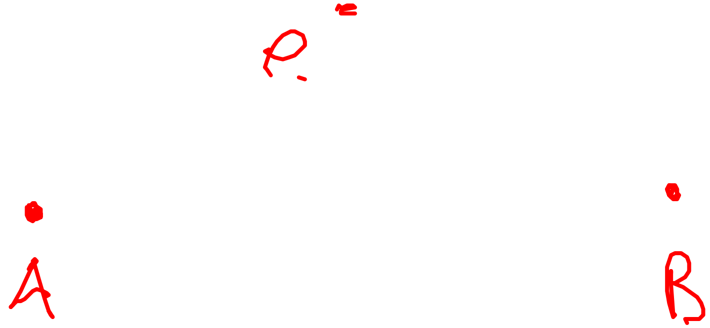
⇒ OPTIMAL α

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

E_α minimum $\Rightarrow \frac{dE}{d\alpha} = 0$

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

Hydrogen Molecular Ion H_2^+



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

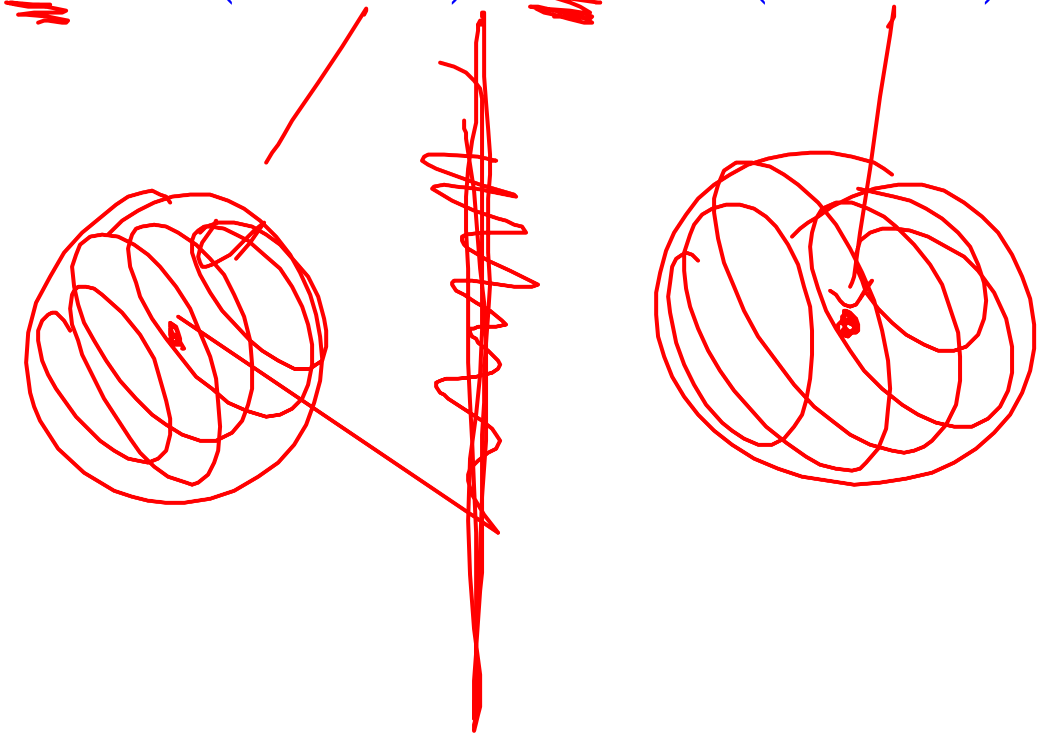
Linear Combination of Atomic Orbitals

- Most common approach to find out the 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:

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

Linear Combination of Atomic Orbitals

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



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