

3.012 Bonding-Structure: Recitation 4 (Solutions)

1 Variational Principle

Solution I

(a) The Hamiltonian of the system is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\widehat{r}) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

(where $m = m_e$)

(b) In atomic units ($\hbar = 1$ a.u., $m = 1$ a.u. of mass, $e = 1$ a.u. of charge, $4\pi\epsilon_0 = 1$ a.u.), the Hamiltonian can be rewritten as: $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$
(the Hamiltonian now appears dimensionless)

(c) The expectation value for the total energy of the trial wavefunction (which we want to minimize with respect to the variational parameter α to obtain the best approximation for the ground-state wavefunction) can be expressed as:

$$E_\alpha = \frac{\langle \psi_\alpha | \hat{H} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \quad (1)$$

$$E_\alpha = \frac{\langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle + \langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \quad (2)$$

The terms in the preceding expression can be calculated as follows:

$$\begin{aligned} \langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle &= -\frac{1}{2} \int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi_\alpha^*(r) \nabla^2 \psi_\alpha(r) r^2 \sin(\theta) dr d\theta d\phi \\ \langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle &= -\frac{1}{2} \int_{r=0}^{r=\infty} \psi_\alpha^*(r) \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \psi_\alpha(r) 4\pi r^2 dr \end{aligned}$$

(from integrals in spherical coordinates)

$$\langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle = -\frac{4\pi C^2}{2} \int_{r=0}^{r=\infty} e^{-\alpha r} \frac{\alpha^2 r^2 - 2\alpha r}{r^2} e^{-\alpha r} r^2 dr$$

$$\begin{aligned}\langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle &= -\frac{4\pi C^2}{2} \int_{r=0}^{r=\infty} (\alpha^2 r^2 - 2\alpha r) e^{-2\alpha r} dr \\ \langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle &= -\frac{4\pi C^2}{2} \left(\alpha^2 \frac{2}{(2\alpha)^3} - 2\alpha \frac{1}{(2\alpha)^2} \right)\end{aligned}$$

(from the expression of $\int_0^{+\infty} r^n e^{-\alpha r} dr$)

As a result:

$$\langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle = +\frac{\pi C^2}{2\alpha} \quad (3)$$

Similarly,

$$\begin{aligned}\langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle &= -\int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi_\alpha^*(r) \frac{1}{r} \psi_\alpha(r) r^2 \sin(\theta) dr d\theta d\phi \\ \langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle &= -4\pi C^2 \int_{r=0}^{r=\infty} e^{-2\alpha r} r dr \\ \langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle &= -4\pi C^2 \frac{1}{(2\alpha)^2} \\ \langle \psi_\alpha | -\frac{1}{r} | \psi_\alpha \rangle &= -\frac{\pi C^2}{\alpha^2}\end{aligned} \quad (4)$$

$$\begin{aligned}\langle \psi_\alpha | \psi_\alpha \rangle &= -\int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi_\alpha^*(r) \psi_\alpha(r) r^2 \sin(\theta) dr d\theta d\phi \\ \langle \psi_\alpha | \psi_\alpha \rangle &= 4\pi C^2 \int_{r=0}^{r=\infty} e^{-2\alpha r} r^2 dr \\ \langle \psi_\alpha | \psi_\alpha \rangle &= 4\pi C^2 \frac{2}{(2\alpha)^3} \\ \langle \psi_\alpha | \psi_\alpha \rangle &= +\frac{\pi C^2}{\alpha^3}\end{aligned} \quad (5)$$

Consequently,

$$E_\alpha = \frac{\frac{\pi C^2}{2\alpha} - \frac{\pi C^2}{\alpha^2}}{\frac{\pi C^2}{\alpha^3}} \quad (6)$$

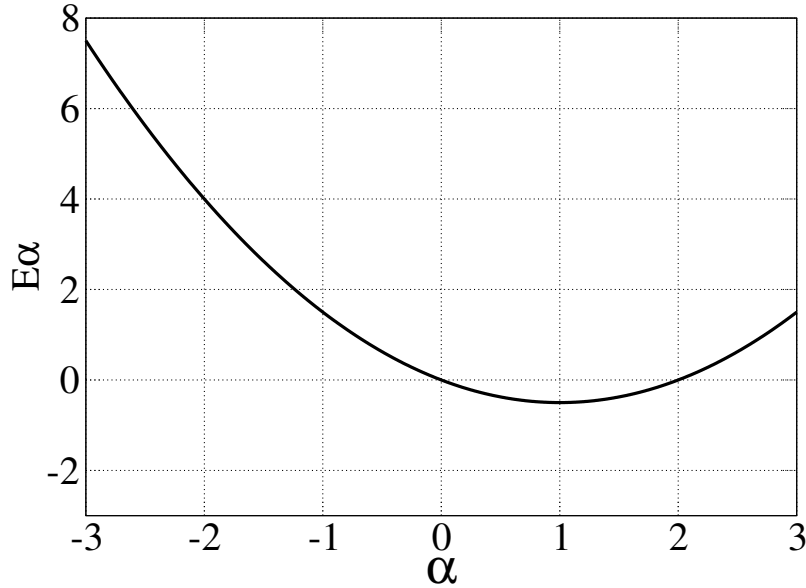
$$E_\alpha = \frac{1}{2}\alpha^2 - \alpha \quad (7)$$

(as expected, the normalization constant C is not involved in this expression)

(d) To obtain the energetically-optimal trial wavefunction, we have to find the value $\alpha = \alpha_{min}$ which minimizes $E_\alpha = \frac{1}{2}\alpha^2 - \alpha$. We solve:

$$\frac{dE_\alpha}{d\alpha} = \alpha - 1 = 0 \quad (8)$$

Thus, $\alpha_{min} = 1$



(e) Minimal energy: $E_{min} = E_{\alpha=1} = -1/2$ a.u. of energy = $-1/2$ Ha = -1 Ryd.

Optimal trial wavefunction: $\psi_{min} = \psi_{\alpha=1} = C e^{-r}$

Normalization condition: $\langle \psi_{min} | \psi_{min} \rangle = 1 = \frac{\pi C^2}{1^3}$

Consequently, $C = \frac{1}{\sqrt{\pi}}$ and $\psi_{min} = \frac{1}{\sqrt{\pi}} e^{-r}$

(f) In atomic units, $E_{1s} = -1/2$ Ha and $\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$, which is in agreement with our results.

This agreement results from the fact that the exact ground-state wavefunction belongs to the selected set of trial wavefunction. If the ground-state wavefunction were not in the initial trial set, we would only obtain an approximation for the ground-state wavefunction ($\psi_{min} \approx \psi_{ground\ state}$) and an approximation for the ground-state energy

($E_{min} \approx E_{ground\ state}$; note that E_{min} is actually an upper bound $E_{min} \geq E_{ground\ state}$)

(e) The potential (in atomic units) is now $-Z/r$ instead of $-1/r$.

Consequently, E_α becomes: $E_\alpha = \frac{\frac{\pi C^2}{2\alpha} - Z \frac{\pi C^2}{\alpha^2}}{\frac{\pi C^2}{\alpha^3}}$.

$E_\alpha = \frac{1}{2}\alpha^2 - Z\alpha$. To obtain the energetically-optimal trial wavefunction, we solve:

$$\frac{dE_\alpha}{d\alpha} = \alpha - Z = 0 \quad (9)$$

Thus, $\alpha_{min} = Z$

$E_{min} = E_{\alpha=1} = -Z^2/2$ a.u. of energy = $-Z^2/2$ Ha = $-Z^2$ Ryd

Optimal trial wavefunction: $\psi_{min} = \psi_{\alpha=Z} = C e^{-Zr}$

Normalization condition: $\langle \psi_{min} | \psi_{min} \rangle = 1 = \frac{\pi C^2}{Z^3}$

Consequently, $C = \frac{1}{\sqrt{\pi}}$ and $\psi_{min} = \frac{Z^{\frac{3}{2}}}{\sqrt{\pi}} e^{-Zr}$.

The preceding results are in agreement with the lowest-energy solution of the Schrödinger equation for hydrogen-like atoms (He^+ , Li^{++} , Be^{+++}): $E_{1s} = -Z^2$ Ryd, $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$.

2 Trends Across the Periodic Table

Solution II

We have seen in Lecture 7 that the arrangement of the chemical elements in the periodic table can be explained by the Pauli exclusion principle and by the *Aufbau* principle. Electrons in atoms occupy electronic shells surrounding the nucleus: the first shell (1s) can accommodate 2 electrons, the second shell (subshell 2s + subshell 2p) can host 2+6=8 electrons (Cf. Lecture 7: “Orbital levels in multi-electron atoms”, “*Aufbau*”). In the case of an hydrogen-like atom, it was shown that the existence of the electronic shells (and electronic subshells) is directly related to the orthogonality condition between the eigenfunctions of the stationary Schrödinger equation.

An electron in a given shell is subjected to competitive electrostatic (Coulomb) interactions: the electrostatic interaction with the nucleus tends to lower its energy and its distance to the nucleus, while the interactions with the other electrons tend to increase the electron energy. Due to these competitive interactions, the electrons are said to “screen” the interaction between the nucleus and the electron under consideration. The electrons

belonging to lower electronic shells tend to do so more effectively than the electrons in the same shell¹. Therefore, the nuclear charge which is effectively seen by an electron increases with the number of electrons occupying the shell. As an illustration, from boron B to carbon C, the effective charge felt by an electron in the outermost shell increases by an amount close to 1, the screening effect between electrons in the same shell being very moderate. Thus, as the number of electrons in a given shell increases, the atomic radius² decreases and the amount of energy needed to remove one of the outermost electrons from the atom (first ionization energy) increases. When the outermost shell is filled (He, Ne, Ar, Kr), the additional electron is constrained to occupy a new shell (one goes from one line of the periodic table to the next) and the atomic radius increases significantly.

We moreover observe some interesting features from Be to B and from Mg to Al. These singularities are due to the transition from one electronic *subshell* to another (we go, for instance, from the $2s$ to the $2p$ subshell). The singularities in the ionization energy from N to O or from P to S are, at this stage, more difficult to rationalize. They are indeed related to the effect of spin-spin interactions (summarized in the so-called “Hund’s rule”³).

¹as a consequence of the Poisson equation

²The covalent radius is half of the distance between two identical atomic nuclei bound to form a molecule.

³It is energetically-favorable for orbitals in an electronic subshell to get occupied with one electron before any of the subshell orbitals becomes doubly-occupied (all electrons in these singly-occupied orbitals have the same spin orientation).