3.012 Bonding-Structure: Recitation 4

1 Variational Principle

Recall

- *International System units, atomic units:*

Quantity	Symbol	Atomic Units	S.I. Units
Hartree	Ha	1 a.u. (of energy)	4.36×10^{-18} J (= 27.2 eV)
electron charge	e	1 a.u. (of charge)	1.60×10^{-19} C
electron mass	m_e	1 a.u. (of mass)	9.11×10^{-31} kg
Bohr Radius	a_0	1 a.u. (of length)	0.529×10^{-10} m
permittivity of free space	ϵ_0	$\frac{1}{4\pi}$ a.u.	8.85×10^{-12} $C^2.N^{-1}.m^{-2}$
Planck's constant	$\hbar$	1 a.u.	1.054×10^{-34} J.s

- *variational principle:*

  goal $\rightarrow$ *find a close approximation for the ground-state wavefunction of a quantum system*

  outline of the method $\rightarrow$ *i) write the Hamiltonian ii) select a set of trial wavefunctions iii) calculate the expectation value for the total energy of each trial wavefunction iv) the wavefunction corresponding to the lowest total energy is the best approximation for the ground state of the system*

- *useful integral*: $\int_0^{+\infty} r^n e^{-\alpha r} dr = n \times (n-1) \times ... \times 2 \times 1 \times \frac{1}{\alpha^{n+1}}$

- *integrals in spherical coordinates:*
  $\int_{space} f(\overrightarrow{r}) d\overrightarrow{r} = \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} f(r,\theta,\phi) r^2 \sin(\theta) dr d\theta d\phi$

Problem I

We consider an electron in the presence of a Hydrogen nucleus H^+.

(a) Write the Hamiltonian of the system in S.I. units.

(b) Write the Hamiltonian of the system in atomic units.

We wish to find an approximation for the ground-state wavefunction of the Hydrogen atom without solving the Schrödinger equation. To this end, we apply the variational principle. We select the following trial wavefunctions: $\psi_\alpha(r) = Ce^{-\alpha r}$ (where α and C are constants).

(c) Calculate E_α, the expectation value for the total energy of an electron in the state ψ_α.

Hint: Using integrals in spherical coordinates and the expression for $\int_0^{+\infty} r^n e^{-\alpha r} dr$, you can show that:

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

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

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

and use these equalities to determine E_α.

(d) Plot E_α in function of α. Determine α_{min}, the value of α for which E_α reaches the minimal value.

(e) Calculate the minimal energy E_{min} (specify your units). Write the corresponding wavefunction ψ_{min} in its normalized form.

(f) Compare your results to the ground-state energy and the ground-state wavefuntions obtained by directly solving the Schrödinger equation: $E_{1s} = -13.60$ eV, $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-r/a_0}$ (pay attention to the units). Why do we obtain such a good agreement?

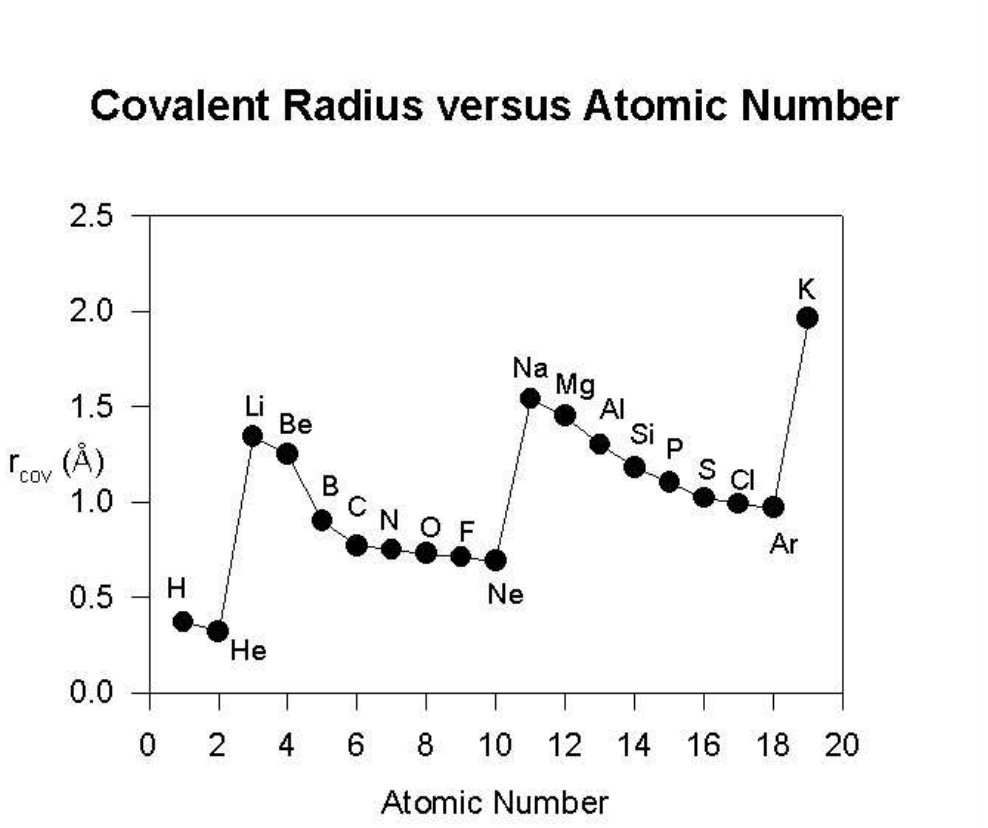
(g) Repeat the variational procedure for an electron in the presence of a nucleus of charge $+Ze$.

2 Trends Across the Periodic Table

Problem II

Explain the following graphs (*hint:* Pauli exculsion principle, *Aufbau* principle, electron screening, orthogonality constraint, electronic shells, effective nuclear charge).

Note: 1 eV = 96.487 kJ/mol



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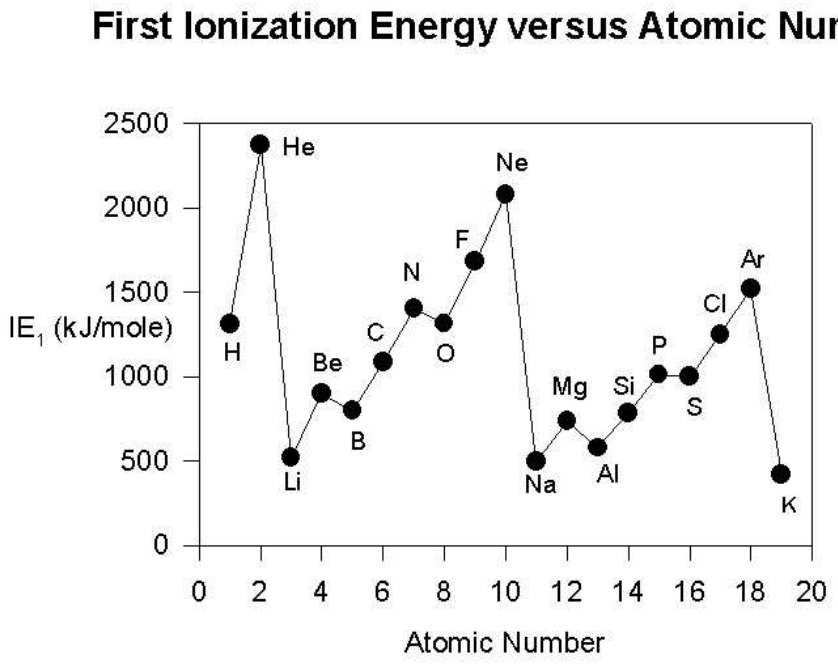

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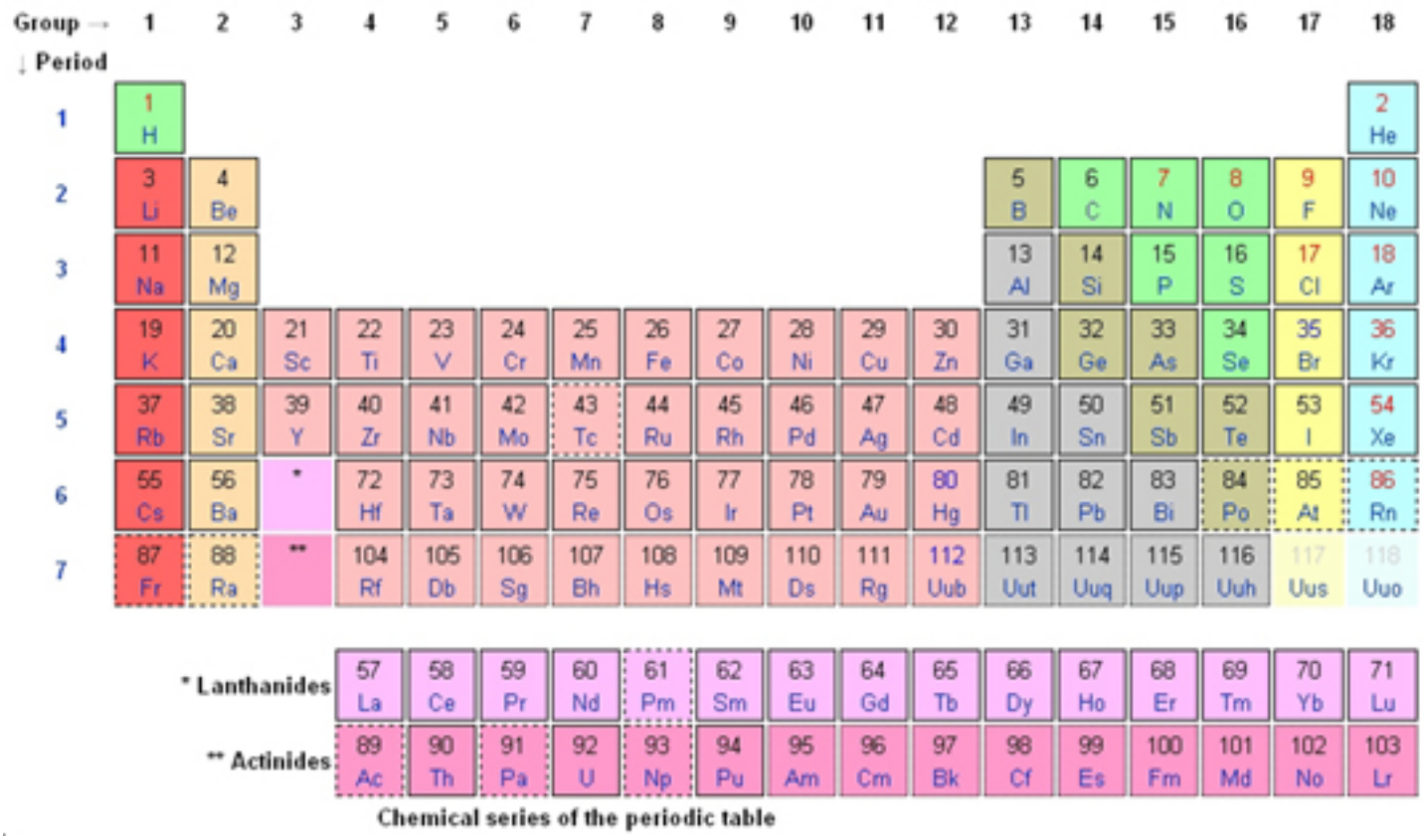

Source: Wikipedia