

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 → find a close approximation for the ground-state wavefunction of a quantum system

outline of the method → 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:* $\int_0^{+\infty} r^n e^{-\alpha r} dr = n \times (n-1) \times \dots \times 2 \times 1 \times \frac{1}{\alpha^{n+1}}$

- *integrals in spherical coordinates:*

$$\int_{space} f(\vec{r}) d\vec{r} = \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} f(r, \theta, \phi) r^2 \sin(\theta) dr d\theta d\phi$$

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 wavefunctions 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 $+Ze$.

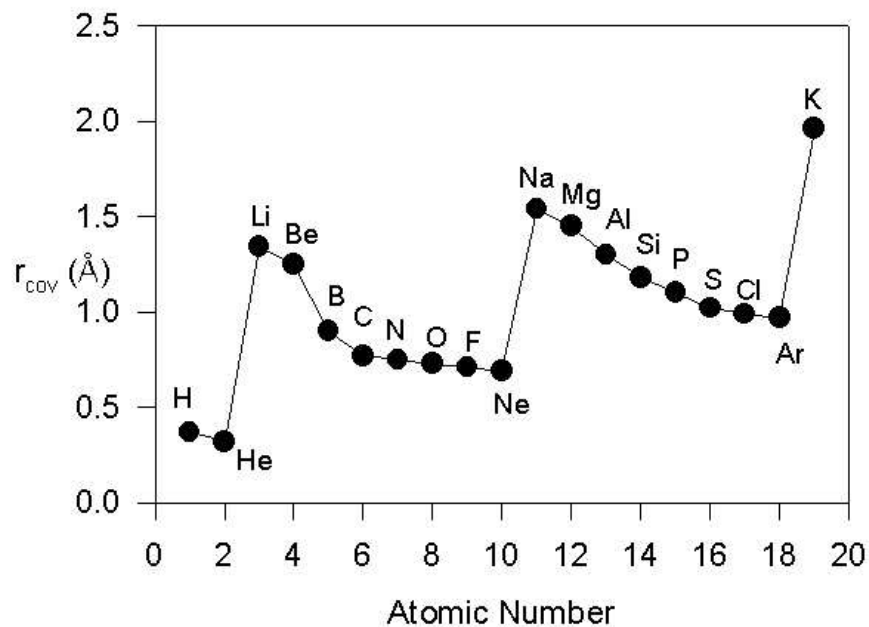
2 Trends Across the Periodic Table

Problem II

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

Note: 1 eV = 96.487 kJ/mol

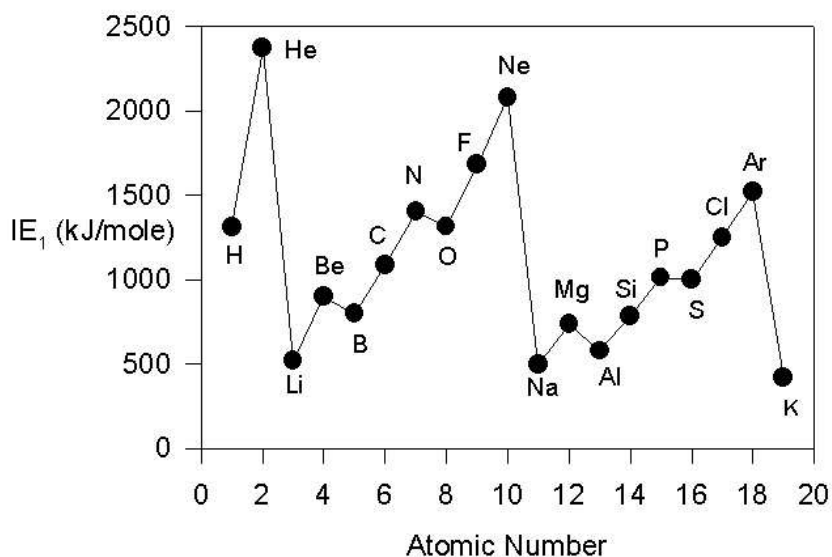
Covalent Radius versus Atomic Number



Courtesy of Professor W. Rodger Nutt. Used with permission.

source: http://www.chm.davidson.edu/ronutt/che115/cv_ie_ea.htm

First Ionization Energy versus Atomic Number



Courtesy of Professor W. Rodger Nutt. Used with permission.

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanides			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
** Actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Chemical series of the periodic table

Source: Wikipedia