10.6 Summary of important relations

Radius of an atom

$$r_a = \overline{r}_a(Z)\,a_B, \quad 1 < \overline{r}_a(Z) < 5; \qquad a_B = \frac{\hbar^2}{m_e e^2} = 0.529\,\text{A} \tag{10.2}$$

Energy levels in the hydrogen atom

$$\varepsilon_{n-1} \approx -\frac{e^2}{2a_B}\frac{1}{n^2} \approx -13.6\frac{1}{n^2}\,\text{eV}, \;\; n = 1, 2, 3, ... \tag{10.1}$$

Energy ordering of levels in atoms other than the hydrogen

$$\varepsilon_{n\ell} < \varepsilon_{n\ell'}, \text{ if } \; \ell < \ell', \quad n\text{=2, 3, 4,}\dots \tag{10.4a}$$

$$\varepsilon_{n+2,s} \approx \varepsilon_{n+1,\text{d}} \approx \varepsilon_{n,\text{f}}, < \varepsilon_{n+2,p}, \quad n = 2,3,4,... \tag{10.4b}$$

$$\varepsilon_{n,s} < \varepsilon_{n,\text{p}} < \varepsilon_{n+1,s}, \qquad n = 2,3,4,... \tag{10.4c}$$

First Ionization energy

$$I_P = \overline{I}'_P(Z)\frac{e^2}{a_B}, \;\; 0.14 < \overline{I}'_P(Z) < 0.9; \qquad \frac{e^2}{a_B} \equiv \frac{\hbar^2}{m_e\, a_B^2} \equiv \frac{e^4 m_e}{\hbar^2} = 27.2\,\text{eV} \tag{10.3}$$

Electron affinity of an atom is the first ionization potential of its -1 anion (if such an anion is formed). The concept is most relevant for halogens. For hydrogen it is about 0.75 eV, which means that the proton can bind two electrons; to extract one of them a minimum of 0.75 eV is needed, while to extract the one left behind a minimum of 13.6 eV is needed.

10.7 Multiple-choice questions/statements

1. One of the following formulae for the ground state energy of the hydrogen atom is wrong. Which one?

(a) $-e^2/2a_B$ (b) $-e^4/2m_e\hbar^2$ (c) $-e^4 m_e/2\hbar^2$ (d) $-\hbar^2/2m_e a_B^2$

2. The average value of the kinetic energy $\langle n,l,m|(p^2/2m_e)|n,l,m\rangle$ in the hydrogen atom is: (*We clarify that* $\langle n,l,m|$ *and* $|n,l,m\rangle$ *are alternative ways of writing* ψ^*_{nlm} *and* ψ_{nlm} *respectively;* $\langle n,l,m|A|n,l,m\rangle$ *is an alternative way of writing the integral* $\int \psi^*_{nlm}(A\psi_{nlm})d^3r$ *, where A is the operator corresponding to the physical quantity A*).

(a) $\hbar^2/2m_e a_B^2 n^2$ (b) $e^2/a_B n^2$ (c) $e^4 m_e/4\hbar^2 n^2$ (d) $e^4 m_e/\hbar^2 n^2$

3. The average value of the total energy for the ground state of the positronium atom $(e,\, e^+)$ is:

(a) $-\hbar^2/2m_e a_B^2$ (b) $-e^2/2a_B$ (c) $-e^4 m_e/\hbar^2$ (d) $-\hbar^2/4m_e a_B^2$; $\quad a_B \equiv \hbar^2/m_e e^2$

4. The average value of the potential energy in the ground state of the $(p,\, \mu^-)$ atom is: (The mass of μ^- equals $207\,m_e$, $\; a_B \equiv \hbar^2/m_e e^2$)

(a) $-207e^2/a_B$ (b) $-207\hbar^2/2m_e a_B^2$ (c) $-186e^4 m_e/\hbar^2$ (d) $-186e^2/2a_B$

5. The first ionization energy of the $(p,\,\mu^-)$ atom is: (The mass of μ^- equals $207\,m_e$, $a_B \equiv \hbar^2/m_e e^2$)

(a) $93e^4 m_e/\hbar^2$ (b) $186e^2/a_B$ (c) $207\hbar^2/2m_e a_B^2$ (d) $207e^2/2a_B$

6. The first ionization energy of the He atom is approximately (in eV):

(a) 13.6 (b) 24 (c) 27.2 (δ) 54.4

7. The first ionization energy of the Li atom is approximately (in eV):

(a) 13.6 (b) 5 (c) 10 (d) 14

8. The electron affinity of the Cl atom is approximately (in eV):

(a) 13.6 (b) 27.2 (c) 3.6 (d) 54.4

9. The electronic configuration of the C atom is:

(a) $1s^2 2s^2 2p^2$ (b) $2s^2 2p^4$ (c) $1s^1 2s^1 2p^1 3s^1 3p^1 3d^1$ (d) $1s^2 2p^4$

10. The electronic configuration of the O atom is:

(a) $2s^2 2p^6$ (b) $1s^4 1p^4$ (c) $1s^2 2p^6$ (d) $1s^2 2s^2 2p^4$

11. The electronic configuration of the Cu is:

(a) $[\mathrm{Ar}]3d^{10}4s^1$ (b) $[\mathrm{Ar}]3d^9 4s^1 4p^1$ (c) $[\mathrm{Ar}]3d^8 4s^1 4p^2$ (d) $[\mathrm{Ar}]3d^{11}$

12. The angular dependence of the p_x orbital is:

(a) $\sin^2\theta$ (b) $\sin\theta\sin\phi$ (c) $\sin\theta\cos\varphi$ (d) $\cos\theta$

13. The angular dependence of the d_{zx} orbital is:

(a) $\cos^2\theta$ (b) $\cos\theta\sin\theta\cos\varphi$ (c) $\sin^2\varphi\sin\theta$ (d) $\cos\theta\sin\theta\sin\varphi$

14. The sixth ionization energy of the C atom is about (in eV):

(a) 13.6 (b) 27.2 (c) 81.6 (d) 489.6

15. The fourth line of the periodic table of the elements (PTE) has

(a) 8 (b) 18 (c) 32 (d) 60 elements

16. The element located at the fifth line and the first column of the PTE has

(a) 19 (b) 27 (c) 35 (d) 37 electrons

17. The average value $\langle n,l,m,|r^{-1}|n,l,m\rangle$ of $1/r$ in hydrogen atom is

(a) $1/na_B$ (b) $1/n^2 a_B$ (c) $1/2n^2 a_B$ (d) $1/2na_B$

10.8 Solved problems

1. *Obtain the second and the third ionization energy of Li. It is given that* $\langle 1/r_{12}\rangle = 5/(8a)$, *where a is the radius of the 1s orbital of the system of a Li nucleus plus two electrons in the corresponding 1s orbital.*

Solution: The Hamiltonian of the Li^+ cation consists of the kinetic energy of the two electrons plus the Coulomb interactions. Since the electrons are in a 1s orbital with a radius *a* (to be determined) we have for the average value of the Hamiltonian

$$\langle H\rangle = \frac{\hbar^2}{2m_e a^2} + \frac{\hbar^2}{2m_e a^2} - \frac{Ze^2}{a} - \frac{Ze^2}{a} + \frac{5e^2}{8a}, \quad Z=3 \tag{1}$$

We use the atomic system of units $(\hbar = m_e = e = 1)$ and we set $a = 1/x$ so we have

$$\langle H\rangle = x^2 - (6 - \tfrac{5}{8})x \tag{2}$$

By minimizing (2) we respect to x we obtain $x = 43/16$ and $\langle H\rangle = -(43/16)^2$ or $|\langle H\rangle| = (43/16)^2 \times 27.2 = 196.46$ eV. This is the minimum energy needed to extract the two electrons from the Li^+ cation, i.e. the sum of the second and the third ionization energy of lithium. The third ionization energy is $13.6\times3^2=122.4\text{eV}$. Thus the second ionization energy of lithium is 196.46-122.4=74.06 eV. The experimental values for the second and the third ionization energy are 75.64 eV and 122.45 eV respectively.

2. *Estimate the velocity of an electron being in the orbital 1s of the uranium atom.*

Solution: The kinetic energy $\frac{1}{2}m_e\upsilon^2$ of the electron at the 1s orbital of uranium is approximately Z^2 times that of hydrogen, $\hbar^2Z^2/2m_ea_B^2$, (the Coulomb repulsion of the two electrons occupying the 1s level has been omitted, see problem 1). Thus $\upsilon=Z\hbar/m_ea_B=Zc/137=(92/137)c$. Actually, given that our estimate of this velocity came so close to the velocity of light, we need the relativistic quantum equation of Dirac and not that of Schrödinger (on which our previous estimate was based) to really determine this velocity.

3. *Obtain the electron affinity of hydrogen. It is given that $\langle 1/r_{12}\rangle=35/(64a)$ where a is the radius of the 1s orbital of the system of a proton plus two electrons.*

Solution: The electron affinity of the hydrogen atom is by definition the first ionization energy of the anion of hydrogen. We shall work as in the case of Li^+ cation. The average Hamiltonian is, assuming that both electrons of H^- occupy the 1s orbital with a radius $a=1/x$,

$$\langle H\rangle=x^2-\left(2-\tfrac{35}{64}\right)x \qquad (1)$$

Thus, by minimizing, we have $x=93/128$, $|\langle H\rangle|=(93/128)^2\times27.2=14.358\,\text{eV}$, and the electron affinity is $14.358-13.6=0.758\,\text{eV}$ vs. 0.7542 eV for the experimental value.

10.9 Unsolved problems

1. How much would the density of the human body change if the electron mass were half its present value and everything else remain unchanged?

2. Consider two neutral hydrogen atoms at a distance *R* between their protons, $1\text{fm}<R<20\,\mathring{A}$, $1\mathring{A}=10^{-10}\text{m}$. Plot the energy of this system vs. *R* in a log-log graph omitting the kinetic energy of the protons. Mark the characteristic energies and distances.

3. The experimental value of the 20th ionization energy of calcium is 5469.86 eV. Is your estimate for this ionization potential consistent with the experimental value? If not, what is your explanation for the observed discrepancy?