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Chapter 1

Note: The first printing has a few odd typos, which are indicated in blue below. These will be corrected in the reprint.

1.1 Virial theorem The Li atom has a nucleus with a +3e positive charge, which is surrounded by a full 1s shell with two electrons, and a single valence electron in the outer 2s subshell. The atomic radius of the Li atom is about 0.17 nm. Using the Virial theorem, and assuming that the valence electron sees the nuclear +3e shielded by the two 1s electrons, that is, a net charge of +e, estimate the ionization energy of Li (the energy required to free the 2s electron). Compare this value with the experimental value of 5.39 eV. Suppose that the actual nuclear charge seen by the valence electron is not +e but a little higher, say +1.25e, due to the imperfect shielding provided by the closed 1s shell. What would be the new ionization energy? What is your conclusion?

Solution

First we consider the case when the outermost valence electron can see a net charge of +e. From Coulomb's law we have the potential energy

$$PE = \frac{Q_1Q_2}{4\pi\varepsilon_0 r_0} = \frac{(+e)(-e)}{4\pi\varepsilon_0 r_0}$$

$$= -\frac{(1.6 \times 10^{-19} \text{ C})^2}{4\pi(8.85 \times 10^{-13} \text{ Fm}^{-1})(0.17 \times 10^{-9} \text{ m})} = 1.354 \times 10^{-18} \text{ J or -8.46 eV}$$

Virial theorem relates the overall energy, the average kinetic energy \overline{KE} , and average potential energy \overline{PE} through the relations

$$\overline{E} = \overline{PE} + \overline{KE}$$
 and $\overline{KE} = -\frac{1}{2}\overline{PE}$

Thus using Virial theorem, the total energy is

$$\overline{E} = \frac{1}{2} \overline{PE} = 0.5 \times -8.46 \text{eV} - 4.23 \text{ eV}$$

The ionization energy is therefore 4.23 eV. Now we consider the second case where electron the sees +1.25e due to imperfect shielding. Again the Coulombic PE between +e and +1.25e will be

$$PE = \frac{Q_1 Q_2}{4\pi \epsilon_0 r_0} = \frac{(+1.25e)(-e)}{4\pi \epsilon_0 r_0}$$

$$= -\frac{1.25 \cdot (1.6 \times 10^{-19} \text{ C})^2}{4\pi (85 \times 10^{-12} \text{ Fm}^{-1})(0.17 \times 10^{-9} \text{ m})} = -1.692 \times 10^{-18} \text{ J or } -10.58 \text{ eV}$$

The total energy is,

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Jiyuan Zhang

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