Why atoms don't collapse

Notes on General Chemistry

http://quantum.bu.edu/notes/GeneralChemistry/WhyAtomsDon'tCollapse.pdf
Last updated Friday, November 19, 2004 17:31:11-05:00

Department of Chemistry, Boston University, Boston MA 02215

The balance of kinetic and potential energy in an atom is what keeps its electrons from collapsing into the nucleus. We can see how this balancing works qualitatively as follows, for the example of the ground state of hydrogen atom.

Using the be Broglie relation $p = h/\lambda$ between the momentum $p = m\,u$ of a particle of mass m and speed u and the wavelength λ of the matter wave associated with it, we can express the kinetic energy of the electron as

$$\text{KE} = \frac{1}{2}\,m\,u^2 = \frac{p^2}{2\,m} = \frac{h^2}{2\,m\,\lambda^2}.$$

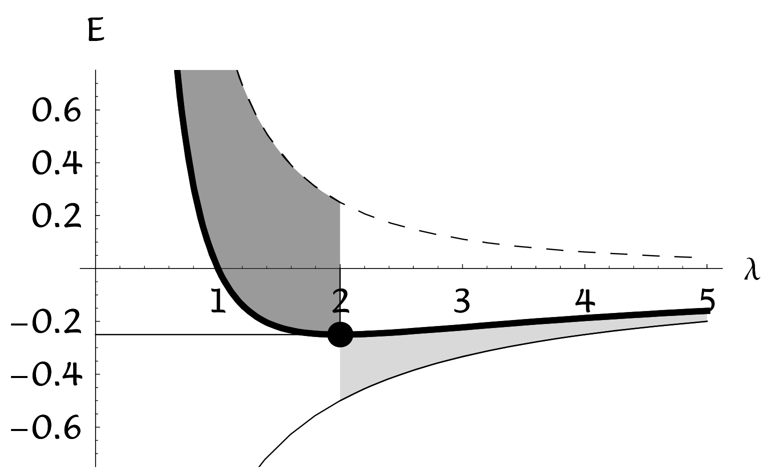
Using Coulomb's law, we can write the potential energy of the electron of charge $-e$ a distance r from a nucleus of charge $+Z\,e$ (Z = 1 for hydrogen atom) as

$$\text{PE} = \frac{(Z\,e)\,(-e)}{4\,\pi\,\epsilon_0\,r} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r} \approx -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,\lambda}$$

In the last expression we interpret the distance r as approximately equal to the matter wave wavelength λ. Combining the expressions for kinetic energy and potential energy, we see that the total energy depends on matter wave wavelength as

$$E = \text{KE} + \text{PE} \propto \frac{1}{\lambda^2} - \frac{1}{\lambda}.$$

This dependence matter wave wavelength is shown in the following figure.



Qualitative dependence of hydrogen atom potential energy (thin curve), kinetic energy (dashed curve), and total energy (thick curve) versus wavelength of the electron matter wave. The attractive force due to potential energy dominates when the atom is large, that is, at larger matter wave wavelengths (light shaded region), while repulsive force due to kinetic energy dominates when the atom is small, that is, at smaller matter wave wavelengths (dark shaded region).

The figure illustrates that when the wavelength of the electron matter wave is small (dark shaded region), and so when the atom is small, the positive kinetic energy contribution dominates, whereas when the wavelength if the electron matter wave is large (light shaded region), and so when the atom is large, the negative potential energy contribution dominates. These opposing contributions balance one another at an intermediate atom size, indicated by the dot on the total energy curve in the figure.

Problems

> 1. Verify that the figure above is correct by making a table of columns λ, KE $= 1/\lambda^2$, PE $= -1/\lambda$, and $E = 1/\lambda^2 - 1/\lambda$ for values of λ between 0.5 and 5 in steps of 0.5, and then plotting KE, PE, and E versus λ on the same axes.

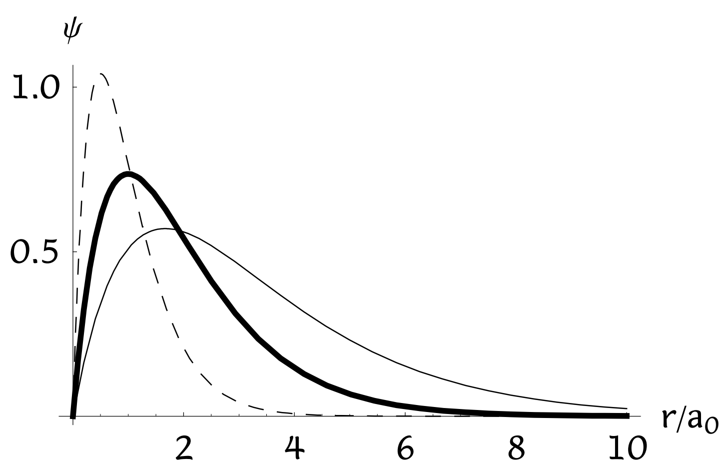
> 2. Show that the value of the total energy $E = 1/\lambda^2 - 1/\lambda$ when $\lambda = \infty$, that is for an atom that is infinitely large is $E = 0$.

> 3. Show that the value of the total energy $E = 1/\lambda^2 - 1/\lambda$ when $\lambda = 0$, that is for an atom that is infinitely small (as a result of collapse of the electron into the nucleus) is $E = +\infty$.

> 4. If you know calculus, show that the minimum in the total energy $E = 1/\lambda^2 - 1/\lambda$ occurs at $\lambda = 2$, the value of λ at which $dE/d\lambda = 0$.

■ Hydrogen atom energy balance

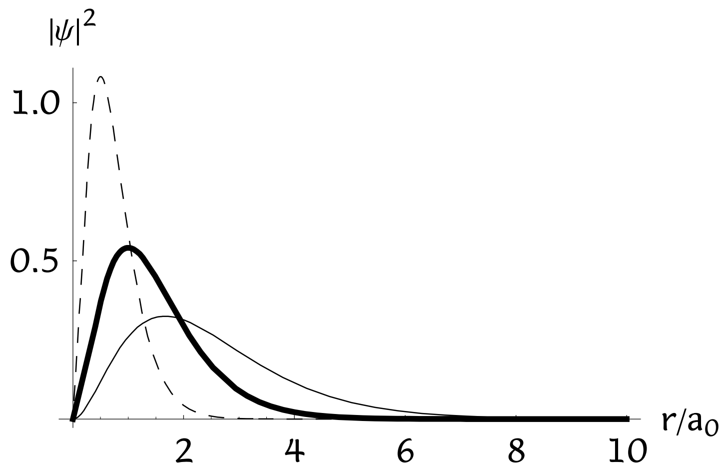
This analysis can be made more exact by taking into account the shape of the electron matter wave. For hydrogen atom in its lowest energy state, the matter wave is spherical. The figure shows alternative hydrogen atom lowest energy spherical matter waves, ψ.



Cross section through alternative hydrogen atom lowest energy spherical waves, ψ. Distance from the nucleus, r, is in units a_0 = 0.529 Å. The thick line is the correct spherical wave; the thin line is a spherical wave that is too diffuse; and the dashed line is a spherical wave that is too compact.

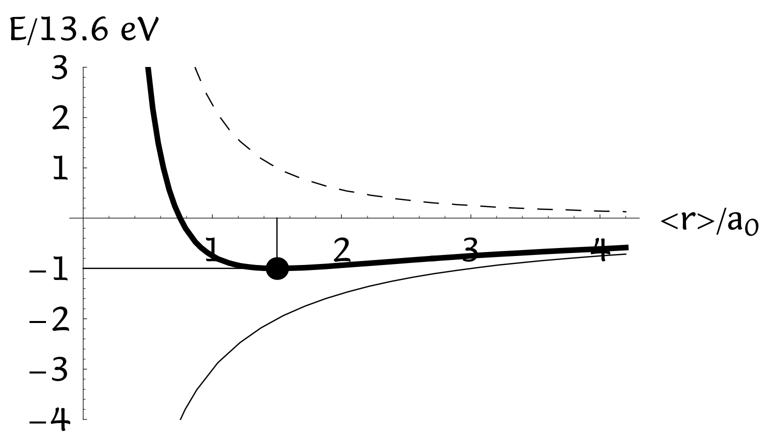
The thick curve is the cross section through the true hydrogen atom ground state matter wave. The other two curves show cross sections through a more diffuse and a more compact matter wave. The wavelength of the matter wave is interpreted to be the average size of the matter wave, denoted as $\langle r \rangle$.

The square of the matter wave determines how the electron is distributed around the atom. Here are these distributions for the three alternative hydrogen atom matter waves above.



Cross section through alternative hydrogen atom lowest energy spatial distributions, $|\psi|^2$. Distance from the nucleus, r, is in units a_0 = 0.529 Å. The thick line is for the correct spherical wave; the thin line is for a spherical wave that is too diffuse; and the dashed line is for a spherical wave that is too compact.

The potential energy and kinetic energy corresponding to a matter wave are computed by weighting their values at each distance from the nucleus by the fraction of the electron at that distance, $|\psi|^2 \, dr$.



Hydrogen atom average potential energy (thin curve), average kinetic energy (dashed curve), and average total energy (thick curve) versus average size $\langle r \rangle$ of the spherical wave of the lowest energy state of the atom. Energy is in units of the ionization energy of hydrogen atom, 13.6 eV, and size in units of the Bohr radius, a_0 = 0.529 Å. The energy minimum at $\langle r \rangle = 1.5$, $E = -1$ is the observed value for hydrogen atom.

Spherical waves for which $\langle r \rangle > 1.5$ are too diffuse and result in potential energies that are too small, the more so the more diffuse the spherical wave. Spherical waves for which $\langle r \rangle < 1.5$ are too compact and result in kinetic energies that are too large, the more so the more compact the spherical wave. It is the increase in kinetic energy that opposes the spherical wave becoming more compact, and so prevents the collapse of the spherical wave into the nucleus. In this way we can understand the stability of the atom against collapse of the electron into the nucleus.

Problems

For hydrogen atom, the total energy minimum, relative to ionized H^+ and e^-, is -1×13.6 eV at an average distance from the nucleus of $1.5 \times 5.29177 \times 10^{-11}$ m, that is 79.3766 pm. The potential energy of an electron separated from the nucleus of charge $+Z\,e$ is

$$\mathrm{PE} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}$$
$$= -\frac{2\,Z}{r} \times 13.6057\,\mathrm{eV} \times 5.29177 \times 10^{-11}\,\mathrm{m} = -\frac{2\,Z}{r} \times 7.19982 \times 10^{-10}\,\mathrm{eV\,m}$$

The righthand side of this expression is obtained using the fact that $e^2/(8\,\pi\,\epsilon_0\,a_0) = 13.6057$ eV, where $a_0 = 5.29177 \times 10^{-11}$ m.

> 5. What is the ionization energy of hydrogen atom, in eV? Answer: 13.6 eV.

> 6. What is the ionization energy of one mole of hydrogen atoms, in kJ/mol? Answer: 1313 kJ/mol.

> 7. Calculate the potential energy in eV of hydrogen atom when the electron is at an average distance of 79.4 pm. Answer: −18.1 eV.

> 8. How much kinetic energy in eV does the hydrogen atom electron have when it is at an average distance of 79.4 pm. Answer: +4.5 eV.

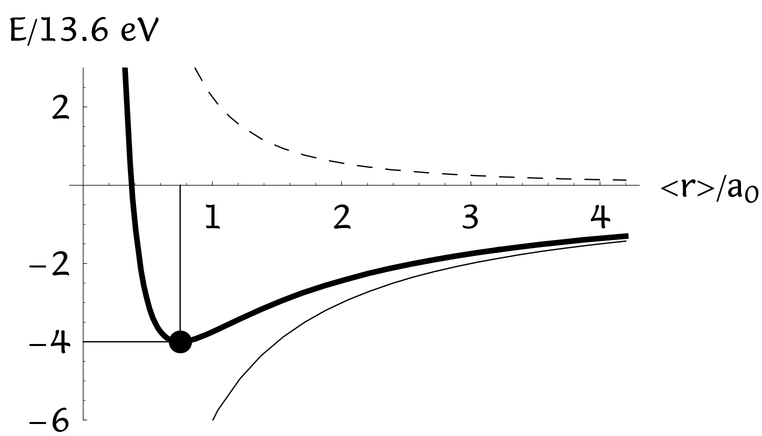
> 9. Draw an energy diagram showing the relation between the hydrogen atom average potential, kinetic and total energy.

■ Helium ion energy balance

The Coulomb attraction of the electron and nucleus is proportional to the atomic number,

$$\mathrm{PE} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r}.$$

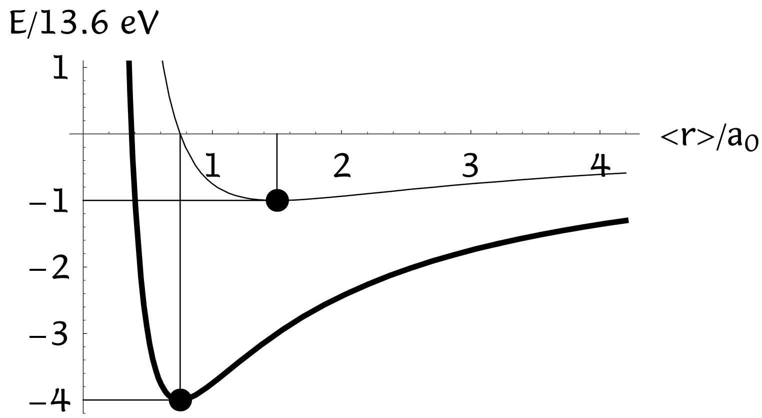
This means the competition between potential and kinetic energy in He^+ should result in a minium total energy that is both deeper, relative to separated He^{2+} and e^-, and closer to the nucleus. Here are the results for the average potential, kinetic and total energies as a functions of the size of He^+.



Helium ion average potential energy (thin curve), average kinetic energy (dashed curve), and average total energy (thick curve) versus average size $\langle r \rangle$ of the spherical wave of the lowest energy state of the ion. Energy is in units of the ionization energy of hydrogen atom, 13.6 eV, and size in units of the Bohr radius, $a_0 = 0.529$ Å. The energy minimum at $\langle r \rangle = 0/75$, $E = -4$ is the observed value for helium ion..

Spherical waves for which $\langle r \rangle > 0.75$ are too diffuse and result in potential energies that are too small, the more so the more diffuse the spherical wave. Spherical waves for which $\langle r \rangle < 0.75$ are too compact and result in kinetic energies that are too large, the more so the more compact the spherical wave. It is the increase in kinetic energy that opposes the spherical wave becoming more compact, and so prevents the collapse of the spherical wave into the nucleus. In this way we can understand the stability of the ion against collapse of the electron into the nucleus.

Here is a comparison of the average total energy of hydrogen atom and helium ion.



Hydrogen atom (thin line) and helium ion (thick line) average total energy (thick curve) versus average size $\langle r \rangle$ of the spherical wave of the lowest energy state. Energy is in units of the ionization energy of hydrogen atom, 13.6 eV, and size in units of the Bohr radius, $a_0 = 0.529$ Å.

Problems

For helium ion, the total energy minimum, relative to ionized He^+ and e^-, is -4×13.6 eV at an average distance from the nucleus of $0.75 \times 5.29177 \times 10^{-11}$ m, that is 39.688 pm.

> 10. Does it seem reasonable that helium ion should be smaller and have a deeper minimum than hydrogen atom?

> 11. What is the ionization energy of helium ion, in eV? Answer: 54.4 eV.

> 12. What is the ionization energy of one mole of helium ions, in kJ/mol? Answer: 5251 kJ/mol.

> 13. Calculate the potential energy in eV of helium ion when the electron is at an average distance of 39.7 pm. Answer: −72.6 eV.

> 14. How much kinetic energy in eV does the helium ion electron have when it is at an average distance of 39.7 pm. Answer: +18.2 eV.

> 15. Draw an energy diagram showing the relation between the helium ion average potential, kinetic and total energy.