

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 21
Oct 29th, 2013

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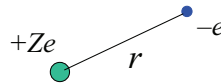
Objectives

- To present the elements needed for the quantum treatment of the hydrogen atom and hydrogenic systems.
- To present the Schrödinger equation for hydrogenic systems and its solutions.
- To introduce the Bohr radius, the Hartree as a unit of energy and the Rydberg constant.
- To compute the ground state and ionization energy for the hydrogen atom.

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The Hydrogen atom and one-electron ions

A **hydrogenic** atom is a two-body system consisting of an electron (charge $-e$) and a nucleus with an atomic number Z (charge $+Ze$)



The electron-nucleus interaction is described by Coulomb's law:

$$\text{Classical force: } F = \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^2}$$

$$\text{Potential energy: } V = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$$

$$F = -\frac{dV}{dr}$$

Here r is the electron-nucleus distance, e is the electron charge, and ϵ_0 is the permittivity of vacuum.

In SI units: $\epsilon_0 = 8.854188 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2 \cdot \text{kg}^{-1} \cdot \text{m}^{-3}$

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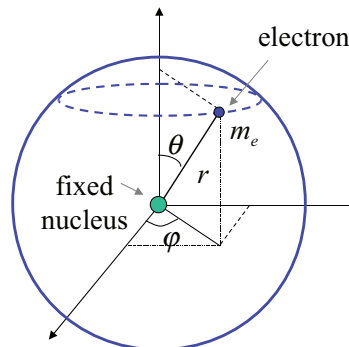
Mathematical description of hydrogenic atoms

The atomic nucleus is much heavier than an electron, so it moves much more slowly than the electron. To a good approximation, one can assume that the nucleus is at rest and only the electron moves. This is called the *fixed-nucleus approximation*.

To treat a hydrogenic atom mathematically, we place the nucleus at the origin and describe the position of the electron using the spherical polar coordinates:

Figure. A hydrogenic atom in the fixed-nucleus approximation.

H atom has $Z = 1$,
 He^+ ion has $Z = 2$,
 Li^{2+} ion has $Z = 3$,
 and so on.



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The Schrödinger equation for hydrogenic atoms

The Schrödinger equation for the electron in a hydrogenic atom is

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi(r, \theta, \varphi) = E \psi(r, \theta, \varphi)$$

When the operator ∇^2 is transformed to the spherical polar coordinates (r, θ, φ) , one obtains the following expression for the kinetic energy operator:

$$\hat{T} = -\frac{\hbar^2}{2m_e} \nabla^2 = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{2m_e r^2} \hat{L}^2$$

Note that the part which depends on θ and φ is identical with the kinetic energy operator for a particle on the surface of a sphere of radius r .

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The Schrödinger equation for the hydrogen atom can be solved by separation of variables

We substitute the above expression for the kinetic energy operator into the Schrödinger equation and multiply the result by $2m_e r^2$ to obtain

$$-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \hat{L}^2 \psi - 2m_e r^2 \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \psi = 0$$

This suggests that ψ has the separable form:

$$\psi(r, \theta, \varphi) = R(r)\Theta(\theta, \varphi)$$

Assuming that the wave function ψ is separable, one can perform a few manipulations and split the original equation for one function of three variables (ψ) into two equations for functions of two and one variable, as described below.

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Equations for the angular and radial parts

Equation for the angular part

$$\hat{L}^2 \Theta(\theta, \varphi) = \lambda \Theta(\theta, \varphi)$$

Its solutions are spherical harmonics

$$\Theta(\theta, \varphi) = Y_l^m(\theta, \varphi), \quad \begin{array}{l} l = 0, 1, 2, \dots \\ m = 0, \pm 1, \pm 2, \dots, \pm l \end{array}$$

with the eigenvalues

$$\lambda = \hbar^2 l(l+1)$$

Equation for the radial part

$$\left[-\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right] R(r) = ER(r)$$

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Eigenvalues of the equation for the radial part

The radial equation is the only new equation one has to solve in order to complete the solution. The procedure is tedious, so we omit it here.

When one actually solves this equations for $E < 0$, it turns out that the solution exists only for certain discrete values of E , namely,

$$E_n = -\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \frac{Z^2}{2n^2} = -\frac{m_e e^4}{4\epsilon_0^2 \hbar^2} \frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \dots$$

Note that E_n does not depend on l or m . However, it turns out that $n > l$ so that l can only assume the values

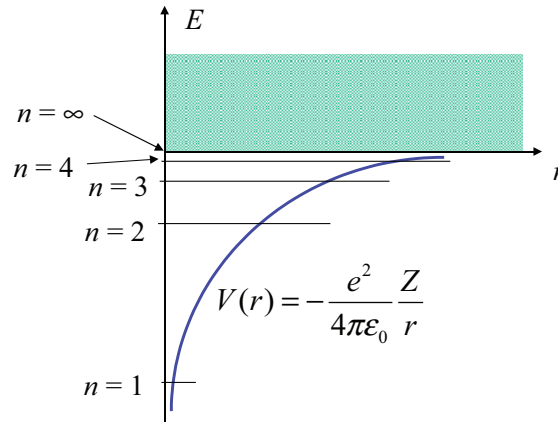
$$l = 0, 1, \dots, n-1$$

For $E > 0$, all energy levels are allowed, i.e., we have a continuum.

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Bound and ionized states of hydrogen-like atoms

Physically, the solutions with $E < 0$ correspond to bound states of the electron in the atom. The solutions with $E > 0$ correspond to states in which the electron has so much kinetic energy that it is not bound to the nucleus, i.e., the atom is ionized.



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The Bohr radius

Consider the following combination of constants

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2} = 5.291772 \times 10^{-11} \text{ m} = 0.5291772 \text{ \AA}$$

This quantity has a dimension of length and is called the **Bohr radius** or the **atomic unit of length**.

In terms of the Bohr radius, the energy levels can be written as

$$E_n = -\frac{\hbar^2}{m_e a_0^2} \frac{Z^2}{2n^2} = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \dots$$

Later we will show that a_0 is the most probable distance between the electron and the nucleus in the H atom.

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Hartree – the atomic unit of energy

Let us consider again the equation

$$E_n = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{2n^2}$$

and define

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{\hbar^2}{m_e a_0^2}$$

E_h is equal to the potential energy of two electrons separated by one Bohr radius

This is a natural unit of energy to use for atoms and molecules; it is called the **Hartree energy** or simply the **hartree**.

In hartree units, the energy of hydrogenlike atoms is given by

$$E_n = -\frac{Z^2}{2n^2} E_h$$

$1 E_h = 27.21138 \text{ eV}$ $1 E_h = 4.359744 \times 10^{-18} \text{ J}$ $1 E_h = 2625.500 \text{ kJ/mol}$
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Beyond the fixed-nucleus approximation

It is actually not necessary to use the fixed-nucleus approximation for hydrogenic atoms. One can show that the two-body problem involving an electron and an nucleus is mathematically equivalent to a one-body problem for a **single fictitious particle of reduced mass μ** moving about the fixed **center of mass** of the two-body system. The reduced mass is

$$\mu = \frac{m_e m_{\text{nucleus}}}{m_e + m_{\text{nucleus}}}$$

If we replace m_e with μ in the Schrödinger equation for this system, we simply need to make the same replacement in all other formulas.

In particular, the energy levels become

$$E_n = -\frac{\mu e^4}{4\epsilon_0^2 \hbar^2} \frac{Z^2}{2n^2}, \quad n = 1, 2, 3, \dots$$

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The reduced mass of a hydrogen-like atoms is very close to the mass of the electron

To obtain the exact agreement with experiment for hydrogenic atoms, one should use the reduced mass μ in place of m_e . Note that

$$m_e = 9.109382 \times 10^{-31} \text{ kg}, \quad m_{\text{proton}} = 1.672622 \times 10^{-27} \text{ kg}$$

$$m_e \ll m_{\text{nucleus}}$$

This means that the reduced mass of a hydrogenlike atom is very close to the mass of the electron:

$$\mu = \frac{m_e m_{\text{nucleus}}}{m_e + m_{\text{nucleus}}} = \frac{m_e}{\frac{m_e}{m_{\text{nucleus}}} + 1} = 0.9994557 m_e \approx m_e$$

For consistency with many-electron atoms, it is customary in quantum chemistry to adopt the **infinite-nuclear-mass approximation** even for the H atom and use m_e instead of μ .

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The Rydberg constant

Another way to express the energy levels of a hydrogenic atom is in terms of wavenumbers:

$$\tilde{\nu}_n = \frac{E_n}{hc} = -\frac{m_e e^4}{4\epsilon_0^2 h^2 (hc)} \frac{Z^2}{2n^2} = -\frac{m_e e^4}{8\epsilon_0^2 h^3 c} \frac{Z^2}{n^2} = -R_\infty \frac{Z^2}{n^2}$$

where R_∞ is the **Rydberg constant** for a nucleus of infinite mass:

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 109737.316 \text{ cm}^{-1}$$

The **Rydberg constant** for the real H atom is

$$R_H = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} = 109677.581 \text{ cm}^{-1}$$

Use R_H when accurate predictions for hydrogenic atoms are needed.

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Electronic transition energies for hydrogenic atoms

Suppose that the electron in a hydrogenic atom “falls” from the state n_1 to n_2 ($n_1 < n_2$). The energy of the emitted photon is

$$\Delta E = E_{n_2} - E_{n_1} = \frac{m_e e^4}{8\epsilon_0^2 h^2} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The wavenumber of the emitted photon is

$$\tilde{\nu}_{n_1 \rightarrow n_2} = \frac{\Delta E}{hc} = R_\infty Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The last formula was first empirically devised by Johannes Rydberg in 1888 to predict the emission lines in the spectrum of the H atom.

In 1913, Niels Bohr proposed a theory of the H atom in which this formula was derived using certain artificial assumptions.

Quantum mechanics gives the same result without such assumptions.

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The emission spectrum of the hydrogen atom

$$\tilde{\nu} = R_H \left(\frac{1}{n_{\text{initial}}^2} - \frac{1}{n_{\text{final}}^2} \right)$$

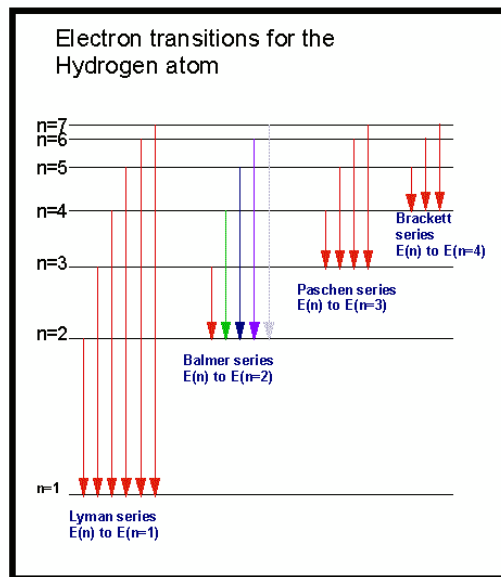
- $n_1 = 1$ Lyman series
- $n_1 = 2$ Balmer series
- $n_1 = 3$ Paschen series
- $n_1 = 4$ Brackett series
- $n_1 = 5$ Pfund series

Selection rules for electronic transitions in hydrogenic atoms:

Δn no restriction

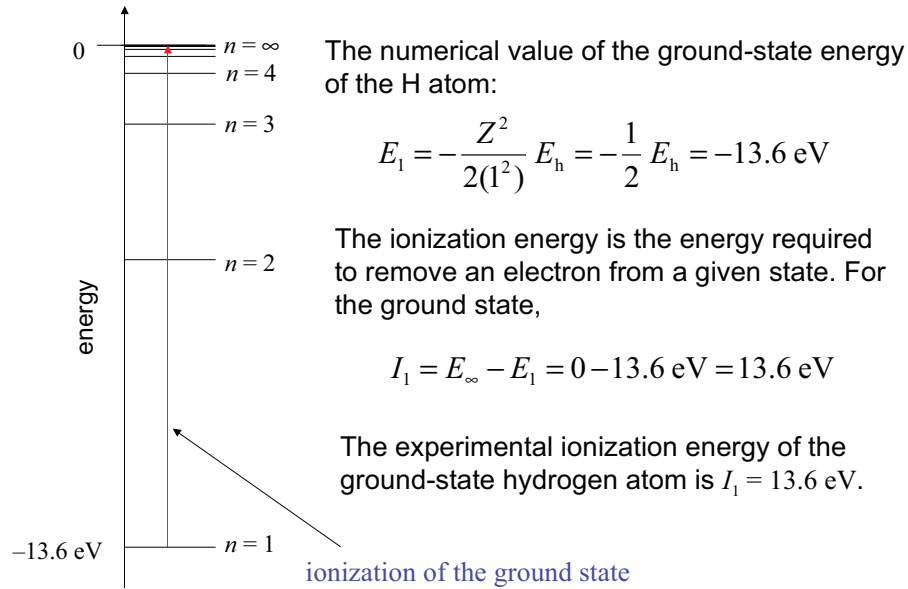
$\Delta l = \pm 1$

$\Delta m = 0, \pm 1$



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The ground state energy and the ionization energy



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Problem. Calculate the wavelength of light emitted when an electron falls from the $n = 100$ orbit to the $n = 99$ orbit of the He^+ ion. Report the answer in centimeters. Assume that the nucleus has an infinite mass.

Solution. The energy levels of a hydrogenic ion may be written as

$$\tilde{\nu}_n = -R_\infty \frac{Z^2}{n^2}$$

where $R_\infty = 109737.316 \text{ cm}^{-1}$

In our case, $Z = 2$. According to the above formula, the wavenumber of the $n = 100 \rightarrow 99$ transition is

$$\tilde{\nu} = \tilde{\nu}_{100} - \tilde{\nu}_{99} = R_\infty Z^2 \left(\frac{1}{99^2} - \frac{1}{100^2} \right) = 0.89124 \text{ cm}^{-1}$$

The corresponding wavelength is

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{0.89124 \text{ cm}^{-1}} = 1.1220 \text{ cm}$$

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