Hydrogen atom

Quantum Chemistry

Lesson 3

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Classical Hamilton function

$$H(\vec{p}_\mathrm{p}, \vec{p}_\mathrm{e}, \vec{r}_\mathrm{p}, \vec{r}_\mathrm{e}) = \frac{1}{2m_\mathrm{p}}\vec{p}_\mathrm{p}^2 + \frac{1}{2m_\mathrm{e}}\vec{p}_\mathrm{e}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left\|\vec{r}_\mathrm{p} - \vec{r}_\mathrm{e}\right\|}$$

- center-of-mass system

$$\vec{R} = \frac{m_\mathrm{p}\vec{r}_\mathrm{p} + m_\mathrm{e}\vec{r}_\mathrm{e}}{m_\mathrm{p} + m_\mathrm{e}}, \quad \vec{r} = \vec{r}_\mathrm{e} - \vec{r}_\mathrm{p}$$

$$H(\vec{P}, \vec{p}, \vec{R}, \vec{r}) = \frac{1}{2M}\vec{P}^2 + \frac{1}{2\mu}\vec{p}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \qquad \left[M = m_\mathrm{p} + m_\mathrm{e}, \mu = \frac{m_\mathrm{p}m_\mathrm{e}}{m_\mathrm{p} + m_\mathrm{e}}\right]$$

- reduced mass

$$\mu = \frac{m_\mathrm{p}m_\mathrm{e}}{m_\mathrm{p} + m_\mathrm{e}} = m_\mathrm{e}\frac{m_\mathrm{p}/m_\mathrm{e}}{1 + m_\mathrm{p}/m_\mathrm{e}} \approx 0{,}9995 m_\mathrm{e} \approx m_\mathrm{e}$$

[wiki]

Classical theory …

Classical Hamilton function

$$H\left(\vec{p}_\mathrm{p}, \vec{p}_\mathrm{e}, \vec{r}_\mathrm{p}, \vec{r}_\mathrm{e}\right) = \frac{1}{2m_\mathrm{p}}\vec{p}_\mathrm{p}^2 + \frac{1}{2m_\mathrm{e}}\vec{p}_\mathrm{e}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left\|\vec{r}_\mathrm{p} - \vec{r}_\mathrm{e}\right\|}$$

- center-o

  - *a uniform rectilinear motion*
  - can be removed by the transition to the CMS

  $\vec{R} = \frac{m_\mathrm{p}\vec{r}_\mathrm{p} \ldots}{m_\mathrm{p} + m_\mathrm{e}}$

$$H\left(\vec{P}, \vec{p}, \vec{R}, \vec{r}\right) = \frac{1}{2M}\vec{P}^2 + \frac{1}{2\mu}\vec{p}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \qquad \left[M = m_\mathrm{p} + m_\mathrm{e}, \mu = \frac{m_\mathrm{p} m_\mathrm{e}}{m_\mathrm{p} + m_\mathrm{e}}\right]$$

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[wiki]

Classical theory …

Classical Hamilton function

$$H(\vec{p}_\mathrm{p}, \vec{p}_\mathrm{e}, \vec{r}_\mathrm{p}, \vec{r}_\mathrm{e}) = \frac{1}{2m_\mathrm{p}}\vec{p}_\mathrm{p}^2 + \frac{1}{2m_\mathrm{e}}\vec{p}_\mathrm{e}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left\|\vec{r}_\mathrm{p} - \vec{r}_\mathrm{e}\right\|}$$

- center-o

  - a uniform
  - can be re

  - motion of a fictitious particle (μ) in a Coulombic field centered in the origin of coordinates

$\vec{R} = \frac{m_\mathrm{p}\vec{r}_\mathrm{p}}{m_\mathrm{p}+m_\mathrm{e}}$

$$H(\vec{P}, \vec{p}, \vec{R}, \vec{r}) = \frac{1}{2M}\vec{P}^2 + \frac{1}{2\mu}\vec{p}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

$\left[M = m_\mathrm{p} + m_\mathrm{e}, \mu = \frac{m_\mathrm{p}m_\mathrm{e}}{m_\mathrm{p}+m_\mathrm{e}}\right]$

- reduced mass

  $\mu = \frac{m_\mathrm{p}m_\mathrm{e}}{m_\mathrm{p}+m_\mathrm{e}} = m_\mathrm{e}\frac{m_\mathrm{p}/m_\mathrm{e}}{1+m_\mathrm{p}/m_\mathrm{e}} \approx 0{,}9995 m_\mathrm{e} \approx m_\mathrm{e}$

[wiki]

Classical theory …

Problem to solve

- system of two particles interacting via a “gravitational” / Coulomb-like potential ($1/r$)
- analytic solutions available
  - conic sections – ellipses (circles), parabolas, hyperbolas
  - bound states – ellipses (circles)

… and semiquantum extensions

Principal failure of the classical theory

- electron (charged particle) emits electromagnetic energy if it moves along a curved trajectory
- the loss of energy → electron must collapse into the atomic nucleus

Bohr model

- circular orbits without any emission
- selected by a quantum constraint imposed on the electron angular momentum (interference destruction of de Broglie waves)

Sommerfeld model

- elliptical orbits

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Quantum theory

Classical Hamilton function (CMS)

$$H(\vec{p},\vec{r}) = \frac{1}{2\mu}\vec{p}^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Hamilton operator (*X*-representation)

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Stationary Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\Delta\Psi(\vec{r}) - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\Psi(\vec{r}) = E\Psi(\vec{r})$$

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Quantum theory

Spherical coordinates

- $x = r \sin\theta \cos\phi,\ y = r \sin\theta \sin\phi,\ z = r \cos\theta$
- $\Delta = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right] = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{1}{r^2}\hat{L}^2$

Important consequences

- $[\Delta, \hat{L}^2] = 0,\ [\Delta, \hat{L}_z] = 0$
- the same holds for the Hamilton operator: $[\hat{H}, \hat{L}^2] = 0,\ [\hat{H}, \hat{L}_z] = 0$
- energy, square of angular momentum, and its projection, (E, L^2, L_z), represent a set of *compatible observables* (complete set)

Solution of the Schrödinger equation (a survey)

Separation of variables

- $\Psi_{klm}(r,\theta,\phi) = R_{klm}(r)Y_{lm}(\theta,\phi)$ $[l = 0,1,2,\dots,\ m = -l, -l+1, \dots, l-1, l]$ *
- $-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\frac{\mathrm{d}}{\mathrm{d}r}R_{kl\cancel{m}}(r)\right] + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]R_{kl\cancel{m}}(r) = E_{kl\cancel{m}}R_{kl\cancel{m}}(r)$

Radial equation

- equation: $R''_{kl} + \frac{2}{r}R'_{kl} + \frac{2\mu}{\hbar^2}\left\{E_{kl} - \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\right\}R_{kl}(r) = 0$
- boundary condition: $\int_0^{+\infty} r^2\, R_{kl}^2(r)\mathrm{d}r < +\infty$

* azimuthal/angular quantum number and magnetic quantum number, respectively

Solution of the Schrödinger equation (a survey)

Modified radial equation

- another substitution $R_{kl}(r) = \chi_{kl}(r)/r$
  - $\chi_{kl}''(r) + \frac{2\mu}{\hbar^2}\left\{E_{kl} - \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\right\}\chi_{kl}(r) = 0$, or $-\frac{\hbar^2}{2\mu}\chi_{kl}'' + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right]\chi_{kl} = E_{kl}\chi_{kl}$
  - $\int_0^{+\infty} \chi_{kl}^2(r)\mathrm{d}r < +\infty$
- effective potential
  - $V_{\mathrm{eff}}(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}$
- (modified) radial equation
  - $-\frac{\hbar^2}{2\mu}\chi_{kl}'' + V_{\mathrm{eff}}\chi_{kl} = E_{kl}\chi_{kl}$ (interpretation!)

Solution of the Schrödinger equation (a survey)

Solution of the radial equation

- $E_{n\not{l}} = -\frac{\mu\gamma^2}{2\hbar^2}\frac{1}{n^2}$, where
  - $\gamma = \frac{e^2}{4\pi\varepsilon_0}$
  - $n = 1,2,3,\ldots$ $(n = n_r + l + 1,\ n_r \geq 0)$ (principal quantum number)
- $R_{nl} \sim \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) e^{-\frac{r}{na_0}}$, where
  - $a_0 = \frac{\hbar^2}{\gamma\mu} \approx 0{,}53 \times 10^{-10}$ m is the Bohr radius
  - L_{n-l-1}^{2l+1} is a generalized Laguerre polynomial, $L_r^s(x) = \frac{1}{r!}e^x x^{-s}\frac{\mathrm{d}^r}{\mathrm{d}x^r}\left(e^{-x}x^{r+s}\right)$
  - $l = 0, 1, \ldots, n-1$ (azimuthal quantum number)
  - $m = -l, -l+1, \ldots, l-1, l$ (magnetic quantum number)

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Summary

Hydrogen atom eigenfunctions

- $\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \sim \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) e^{-\frac{r}{na_0}} P_l^m(\cos\theta)e^{im\phi}$

Energetic spectrum

- $E_n = -\frac{I_p}{n^2}$, $I_p = \frac{\mu\gamma^2}{2\hbar^2} \approx 13{,}6\ \text{eV}$ (ionization potential)
- degenerate energetic levels
  - for a given *n*, totally $\sum_{l=0}^{n-1}(2l+1) = n^2$ (orbital) states ($\times 2$ – spin states – Mendeleev table of elements)
- notation: nl, $n = 1, 2, 3, \ldots$ and $l = \mathrm{s}, \mathrm{p}, \mathrm{d}, \ldots$ (1s, 2s, 2p, ...)

Other hydrogen-like atomic systems

The solution found for the hydrogen atom can straightforwardly be utilized in the cases of

- hydrogen isotopes (deuterium, tritium)
- atomic ions with an electron (He^+, Li^{2+}, ...)
  - $E_n = -\frac{\mu\gamma_Z^2}{2\hbar^2}\frac{1}{n^2}$, where $\gamma_Z = \frac{Ze^2}{4\pi\varepsilon_0}$
  - $R_{nl} \sim \left(\frac{2r}{na_{0Z}}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_{0Z}}\right) e^{-\frac{r}{na_{0Z}}}$, where $a_{0Z} = \frac{\hbar^2}{\gamma_Z\,\mu} \approx \frac{0{,}53\times10^{-10}}{Z}$ m (radius of the Bohr ground-state orbit of particular ion)
- other two-particle systems with particles interacting via a Coulomb-like ($1/r$) potential (electron-positron pair, muonic atom)

The end of lesson 3.