Introduction to Quantum Physics

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Abstract

The video channel with the title “Professor M does Science” in YouTube offers a simple step-by-step but all the same very valuable and rigorous introduction into the world of quantum physics. This script covers the hydrogen atom and helps to digest the topic covered by a group of those videos but is not meant as a replacement for them.

6 Interacting Particles and the Hydrogen Atom

6.1 Relative Motion of Two Interacting Quantum Particles

A particle at position $\underline{r}_1$ with mass m_1 and a particle at position $\underline{r}_2$ with mass m_2 interact via a potential $V = V(\underline{r}_1 - \underline{r}_2)$ that only depends on the relative position of the two particles. In quantum mechanics, the first particle has position $\hat{\underline{r}}_1 = (\hat{x}_1, \hat{y}_1, \hat{z}_1)$ and momentum $\hat{\underline{p}}_1 = (\hat{p}_{x1}, \hat{p}_{y1}, \hat{p}_{z1})$ with the commutation relations $[\hat{x}_1, \hat{p}_{x1}] = i\hbar$, $[\hat{y}_1, \hat{p}_{y1}] = i\hbar$, $[\hat{z}_1, \hat{p}_{z1}] = i\hbar$, and similarly for the second particle.

The center of mass coordinates $\hat{\underline{R}}$ and the relative coordinates $\hat{\underline{r}}$ are defined as

$$\hat{\underline{R}} = \frac{m_1\hat{\underline{r}}_1 + m_2\hat{\underline{r}}_2}{m_1 + m_2} = (\hat{X}, \hat{Y}, \hat{Z}) \qquad\qquad \hat{\underline{r}} = \hat{\underline{r}}_1 - \hat{\underline{r}}_2 = (\hat{x}, \hat{y}, \hat{z}) \tag{6.1}$$

and the original coordinates $\hat{\underline{r}}_1$ and $\hat{\underline{r}}_2$ can be written as

$$\hat{\underline{r}}_1 = \hat{\underline{R}} + \frac{m_2}{m_1 + m_2}\hat{\underline{r}} \qquad\qquad \hat{\underline{r}}_2 = \hat{\underline{R}} - \frac{m_1}{m_1 + m_2}\hat{\underline{r}}$$

in terms of $\hat{\underline{R}}$ and $\hat{\underline{r}}$.

Classically, the total momentum is

$$\underline{P} = M\,\dot{\underline{R}} = (m_1 + m_2)\frac{m_1\dot{\underline{r}}_1 + m_2\dot{\underline{r}}_2}{m_1 + m_2} = m_1\dot{\underline{r}}_1 + m_2\dot{\underline{r}}_2 = \underline{p}_1 + \underline{p}_2$$

in the center of mass coordinates where M is the total mass. It is just the sum of the momenta of the individual particles. The relative momentum is defined as

$$\underline{p} = \mu\,\dot{\underline{r}} = \frac{m_1 m_2}{m_1 + m_2}(\dot{\underline{r}}_1 - \dot{\underline{r}}_2) = \frac{m_2(m_1\dot{\underline{r}}_1) - m_1(m_2\dot{\underline{r}}_2)}{m_1 + m_2} = \frac{m_2\underline{p}_1 - m_1\underline{p}_2}{m_1 + m_2}$$

where μ is called the reduced mass.

In quantum mechanics, the total momentum operator $\hat{\underline{P}}$ and the relative momentum operator $\hat{\underline{p}}$ are defined as

$$\hat{\underline{P}} = \hat{\underline{p}}_1 + \hat{\underline{p}}_2 = (\hat{P}_x, \hat{P}_y, \hat{P}_z) \qquad\qquad \hat{\underline{p}} = \frac{m_2\hat{\underline{p}}_1 - m_1\hat{\underline{p}}_2}{m_1 + m_2} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) \tag{6.2}$$

as in the classical case. The individual $\underline{\hat{p}}_1$ and $\underline{\hat{p}}_2$ momenta can be written as

$$\underline{\hat{p}}_1 = \frac{m_1}{m_1+m_2}\underline{\hat{P}} + \underline{\hat{p}} \qquad\qquad \underline{\hat{p}}_2 = \frac{m_2}{m_1+m_2}\underline{\hat{P}} - \underline{\hat{p}}$$

in terms of $\underline{\hat{P}}$ and $\underline{\hat{p}}$. The commutation relations are

$$\begin{aligned} [\hat{X},\hat{P}_x] = i\hbar \quad [\hat{Y},\hat{P}_y] = i\hbar \quad [\hat{Z},\hat{P}_z] = i\hbar \\ [\hat{x},\hat{p}_x] = i\hbar \quad [\hat{y},\hat{p}_y] = i\hbar \quad [\hat{z},\hat{p}_z] = i\hbar \end{aligned} \tag{6.3}$$

as $[\hat{X},\hat{P}_x] = \frac{1}{m_1+m_2}(m_1([\hat{x}_1,\hat{p}_{x1}] + [\hat{x}_1,\hat{p}_{x2}]) + m_2([\hat{x}_2,\hat{p}_{x1}] + [\hat{x}_2,\hat{p}_{x2}])) = \frac{1}{m_1+m_2}(m_1\, i\hbar + m_2\, i\hbar)$, for example, shows.

The Hamiltonian of the system with the two particles is

$$\hat{H} = \frac{\underline{\hat{p}}_1^2}{2m_1} + \frac{\underline{\hat{p}}_2^2}{2m_2} + V(\underline{\hat{r}}_1 - \underline{\hat{r}}_2)$$

where $\underline{\hat{p}}_1^2$ and $\underline{\hat{p}}_2^2$ can be written as

$$\underline{\hat{p}}_1^2 = \frac{m_1^2}{(m_1+m_2)^2}\underline{\hat{P}}^2 + \underline{\hat{p}}^2 + \frac{2m_1}{m_1+m_2}\underline{\hat{P}}\cdot\underline{\hat{p}} \qquad \underline{\hat{p}}_2^2 = \frac{m_2^2}{(m_1+m_2)^2}\underline{\hat{P}}^2 + \underline{\hat{p}}^2 - \frac{2m_2}{m_1+m_2}\underline{\hat{P}}\cdot\underline{\hat{p}}$$

in terms of the new coordinates. The Hamiltonian becomes

$$\hat{H} = \frac{\underline{\hat{P}}^2}{2M} + \frac{\underline{\hat{p}}^2}{2\mu} + V(\underline{\hat{r}}) \tag{6.4}$$

using $M = m_1 + m_2$ and $\frac{1}{m_1} + \frac{1}{m_2} = \frac{1}{\mu}$. Thus, the system can either be seen as a system of two real particles with mass m_1 and m_2 or as a system of two fictitious particles with mass M and μ. Because the potential only depends on $\underline{\hat{r}}$ the two fictitious particles do not interact, and this makes the problem much simpler. Thus, the Hamiltonian can be separated into two non-interacting terms

$$\hat{H} = \hat{H}_{\text{CoM}} + \hat{H}_{\text{rel}} \qquad \hat{H}_{\text{CoM}} = \frac{\underline{\hat{P}}^2}{2M} \qquad \hat{H}_{\text{rel}} = \frac{\underline{\hat{p}}^2}{2\mu} + V(\underline{\hat{r}})$$

where $\hat{H}_{\text{CoM}}$ is the center of mass Hamiltonian describing the behavior of the center of mass, and $\hat{H}_{\text{rel}}$ is the relative Hamiltonian describing the behavior of a particle that is subject to the potential energy $V(\underline{\hat{r}})$.

The state space $\mathcal{W}_{\text{CoM}}$ for the Hamiltonian $\hat{H}_{\text{CoM}}$ with the eigenvalues E_{CoM} and the eigenstates $|\varphi\rangle_{\text{CoM}}$ as well as the state space $\mathcal{W}_{\text{rel}}$ for the Hamiltonian $\hat{H}_{\text{rel}}$ with the eigenvalues E_{rel} and the eigenstates $|\chi\rangle_{\text{rel}}$ allow to build the state space $\mathcal{W} = \mathcal{W}_{\text{CoM}} \otimes \mathcal{W}_{\text{rel}}$ for the Hamiltonian $\hat{H}$ with the eigenvalue equation $\hat{H}\,|\psi\rangle = E\,|\psi\rangle$. The eigenvalues of $\hat{H}$ are $E = E_{\text{CoM}} + E_{\text{rel}}$ and the eigenstates are $|\psi\rangle = |\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}$. In other words, the two particle system with the Hamiltonian $\hat{H}$ can be solved by finding the solutions for the two one particle systems with the Hamiltonians $\hat{H}_{\text{CoM}}$ and $\hat{H}_{\text{rel}}$, respectively. The eigenvalue equation for $\hat{H}$ is

$$\begin{aligned} \hat{H}\,|\psi\rangle &= \hat{H}(|\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}) = (\hat{H}_{\text{CoM}} \otimes \hat{H}_{\text{rel}})(|\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}) \\ &= E_{\text{CoM}}(|\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}) + E_{\text{rel}}(|\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}) = (E_{\text{CoM}} + E_{\text{rel}})(|\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}) \end{aligned}$$

and it follows $E = E_{\text{CoM}} + E_{\text{rel}}$ and $|\psi\rangle = |\varphi\rangle_{\text{CoM}} \otimes |\chi\rangle_{\text{rel}}$ such that the two Hamiltonians can be solved independently.

The Hamiltonian $\hat{H}_{\text{CoM}}$ becomes

$$\hat{H}_{\text{CoM}} = \frac{\underline{\hat{P}}^2}{2M} \to -\frac{\hbar^2}{2M}\nabla^2_{\text{CoM}} \qquad\qquad \nabla_{\text{CoM}} = \left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z}\right) \tag{6.5}$$

in position representation and has

$$-\frac{\hbar^2}{2M}\nabla^2_{\text{CoM}}\,\varphi_{\text{CoM}}(\underline{R}) = E_{\text{CoM}}\,\varphi_{\text{CoM}}(\underline{R}) \qquad \varphi_{\text{CoM}}(\underline{R}) = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\,\underline{P}\cdot\underline{R}/\hbar} \qquad E_{\text{CoM}} = \frac{\underline{P}^2}{2M}$$

as the eigenvalue equation and its solution because the fictitious particle of the center of mass is a free particle whose solutions are plane waves with a continuous spectrum of energy eigenvalues.

The Hamiltonian $\hat{H}_{\text{rel}}$ becomes

$$\hat{H}_{\text{rel}} = \frac{\hat{\underline{p}}^2}{2\mu} + V(\hat{\underline{r}}) \to -\frac{\hbar^2}{2\mu}\nabla^2_{\text{rel}} + V(\hat{\underline{r}}) \qquad \nabla_{\text{rel}} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{6.6}$$

in position representation and has

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\text{rel}} + V(\hat{\underline{r}})\right]\chi_{\text{rel}}(\underline{r}) = E_{\text{rel}}\,\chi_{\text{rel}}(\underline{r})$$

as the eigenvalue equation. There is no general solution because it depends on the form of the potential $V(\hat{\underline{r}})$. However, there is a general solution in the special case where the potential only depends on their relative distance such that $V(\underline{r}) = V(r)$ where $r = |\underline{r}|$. This is the central potential, and the Coulomb potential is an example.

6.2 Properties of the Hydrogen Atom

Hydrogen is the simplest of all elements as it consists of a single proton and a single electron. It makes up in the order of 74% of all baryonic matter in the universe. It is also important because it is one of the few quantum systems one can solve analytically. The proton has a mass $m_p = 1.67 \cdot 10^{-27}\,\text{kg}$ and an electric charge $e = q_p = 1.60 \cdot 10^{-19}\,\text{C}$. The electron has a mass $m_e = 9.11 \cdot 10^{-31}\,\text{kg}$ and an electric charge $-e = q_e = -1.60 \cdot 10^{-19}\,\text{C}$. Thus, the mass ratio is $m_p/m_e = 1\,833$, and the situation can be seen conceptually as an electron in the field of a proton. For other elements like He, Li, and so on the mass ratio between nucleus and electrons is even larger, and there exist only approximate solutions (the Born-Oppenheimer approximations) for them.

As classical particles, the position of the proton is $\underline{r}_p$ and the position of the electron is $\underline{r}_e$. The Coulomb potential is

$$V(\underline{r}_p, \underline{r}_e) = \frac{1}{4\pi\varepsilon_0}\frac{q_p\,q_e}{\left|\underline{r}_p - \underline{r}_e\right|} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|\underline{r}_p - \underline{r}_e\right|}$$

where ε_0 is the vacuum permittivity. As quantum particles, the potential becomes an operator

$$V(\hat{\underline{r}}_p, \hat{\underline{r}}_e) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|\hat{\underline{r}}_p - \hat{\underline{r}}_e\right|}$$

such that

$$\hat{H} = \frac{\hat{\underline{p}}_p^2}{2m_p} + \frac{\hat{\underline{p}}_e^2}{2m_e} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|\hat{\underline{r}}_p - \hat{\underline{r}}_e\right|} \tag{6.7}$$

is the non-relativistic Hamiltonian of the hydrogen atom. The hydrogen atom is a weakly relativistic system, and there are measurable relativistic terms called fine structure and hyperfine structure but they are ignored here.

The coordinates are replaced

$$(\hat{\underline{r}}_p, \hat{\underline{p}}_p), (\hat{\underline{r}}_e, \hat{\underline{p}}_e) \to (\hat{\underline{R}}, \hat{\underline{P}})(\hat{\underline{r}}, \hat{\underline{p}})$$

following the approach shown for the relative motion of two interacting particles with (6.1) and (6.2) where the first particle is the proton and the second particle is the electron.

The Hamiltonian (6.7) can be written as

$$\hat{H} = \frac{\underline{\hat{P}}^2}{2M} + \frac{\underline{\hat{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\underline{\hat{r}}|} = \hat{H}_{\text{CoM}} + \hat{H}_{\text{rel}} \qquad \hat{H}_{\text{CoM}} = \frac{\underline{\hat{P}}^2}{2M} \qquad \hat{H}_{\text{rel}} = \frac{\underline{\hat{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\underline{\hat{r}}|}$$

according to (6.4) separated into a center of mass Hamiltonian and a relative Hamiltonian. The center of mass Hamiltonian represents a free particle, and the center of mass can therefore be assumed to be stationary without loss of generality. The interesting physics of the hydrogen atom are captured by the relative Hamiltonian $\hat{H}_{\text{rel}}$.

The position of the center of mass in (6.1) can be approximated as

$$\underline{\hat{R}} = \frac{m_p\underline{\hat{r}}_p + m_e\underline{\hat{r}}_e}{m_p + m_e} \approx \frac{m_p\underline{\hat{r}}_p + m_e\underline{\hat{r}}_e}{m_p} = \underline{\hat{r}}_p + \frac{m_e}{m_p}\underline{\hat{r}}_e \approx \underline{\hat{r}}_p + 10^{-3}\underline{\hat{r}}_e \approx \underline{\hat{r}}_p$$

because of the large mass difference between the proton and the electron. The reduced mass μ can be approximated similarly as

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \approx \frac{1}{m_e} \qquad\qquad \mu \approx m_e$$

because $m_p \gg m_e$. Thus, the hydrogen atom is almost equal to an electron moving about a stationary proton.

6.3 Power Series Solution of the Hydrogen Atom

In order to solve the Hamiltonian of the hydrogen atom (6.7) it is sufficient to solve the relative Hamiltonian

$$\hat{H}_{\text{rel}} = \frac{\underline{\hat{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\underline{\hat{r}}|} \qquad \frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \qquad \underline{\hat{p}} = \frac{m_e\underline{\hat{p}}_p - m_p\underline{\hat{p}}_e}{m_p + m_e} \qquad \underline{\hat{r}} = \underline{\hat{r}}_p - \underline{\hat{r}}_e \tag{6.8}$$

with the corresponding eigenvalue equation for the Hamiltonian (6.6) from now on just called $\hat{H}$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{\text{rel}} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\right] - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

in the position representation with spherical coordinates. The potential is a central potential, and therefore results from above can be used. Because of the mass difference between a proton and an electron this relative Hamiltonian can be interpreted approximately as describing the motion of an electron in an electrostatic potential generated by a stationary proton.

Thus, the task is to solve the eigenvalue equation $\hat{H}\,\psi(\underline{r}) = E\,\psi(\underline{r})$. The eigenfunctions of the Hamiltonian can be chosen to also be eigenfunctions of $\underline{\hat{L}}^2$ and $\hat{L}_z$

$$\hat{H}\,\psi(\underline{r}) = E\,\psi(\underline{r}) \qquad \underline{\hat{L}}^2\,\psi(\underline{r}) = \ell(\ell+1)\hbar^2\,\psi(\underline{r}) \qquad \hat{L}_z\,\psi(\underline{r}) = m_\ell\hbar\,\psi(\underline{r})$$

because the Hamiltonian commutes with the angular momentum operators. The eigenvalue ℓ can only take integer values $\ell = 0, 1, 2, 3, ...$, and the eigenvalue m_ℓ can only take values $m_\ell = -\ell, -\ell+1, ..., \ell$ in integer steps. The common eigenfunctions $\psi(\underline{r})$ can be labeled by three quantum numbers k, ℓ, m_ℓ as $\psi_{k\ell m_\ell}(\underline{r})$ where k describes the energy spectrum for a given ℓ and m_ℓ. The energy eigenvalues can be labeled as $E_{k\ell}$.

The solutions of the eigenvalue equations are $\psi_{k\ell m_\ell}(\underline{r}) = R_{k\ell}(r)\,Y_\ell^{m_\ell}(\theta,\varphi)$ where the angular part $Y_\ell^{m_\ell}(\theta,\varphi)$ of the eigenfunctions has the spherical harmonics as its solution, and the spherical harmonics are the same for any central potential. Thus, one part of the problem has been solved.

The other part $R_{k\ell}(r)$ of the eigenfunctions is called the radial part. This is the most interesting part because it depends on the central potential. The eigenvalue equation is

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\ell(\ell+1)\hbar^2}{2\mu\,r^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]R_{k\ell}(r) = E_{k\ell}\,R_{k\ell}(r)$$

and becomes with the substitution $R_{k\ell}(r) = \frac{1}{r} u_{k\ell}(r)$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu\, r^2} - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} \right] u_{k\ell}(r) = E_{k\ell}\, u_{k\ell}(r)$$

where the boundary condition is $u_{k\ell}(0) = 0$. This equation can be interpreted as a particle in one dimension with an energy consisting of a kinetic energy and an effective potential $V_{\text{eff}}(r)$. It has different forms depending on ℓ but all of them approach zero asymptotically from below as $r \to \infty$.

For positive energies $E > 0$ the quantum states are unbound, the energy spectrum is continuous, and the eigenfunctions are not square integrable. For negative energies $E < 0$ the quantum states are bound, the energy spectrum is discrete, and the eigenfunctions are square integrable functions that vanish as r becomes large. The focus here is on the negative energy eigenvalues.

Two values

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu\, e^2} \qquad\qquad E_{\mathrm{I}} = \frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \tag{6.9}$$

where a_0 is called the *reduced Bohr radius* with units of length and E_{I} is called *ionization energy* with units of energy are introduced to simplify notation but both values have also a physical meaning. The differential equation becomes

$$\left[a_0^2 \frac{d^2}{dr^2} - a_0^2 \frac{\ell(\ell+1)}{r^2} + 2a_0 \frac{1}{r} + \frac{E_{k\ell}}{E_{\mathrm{I}}} \right] u_{k\ell}(r) = 0$$

with the eigenvalue $E_{k\ell}$ moved to the left side. Two further simplifications lead to the differential equation

$$\left[\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{k\ell}^2 \right] u_{k\ell}(\rho) = 0 \qquad\qquad \rho = \frac{r}{a_0} \qquad\qquad \lambda_{k\ell} = \sqrt{-\frac{E_{k\ell}}{E_{\mathrm{I}}}}$$

where the minus sign in $\lambda_{k\ell}$ ensures that this value is real for $E_{k\ell} < 0$. This simplifications use the reduced Bohr radius as the unit of length and the ionization energy as the unit of energy.

To solve this equation the limit $\rho \to \infty$ with the differential equation

$$\left[\frac{d^2}{d\rho^2} - \lambda_{k\ell}^2 \right] u_{k\ell}(\rho) = 0$$

is examined first. This is a standard second order linear homogeneous differential equation with the two solutions $u_{k\ell}(\rho) = e^{\pm\lambda_{k\ell}\rho}$. Thus, the solutions in the limit of large values of ρ behave like exponentials. For the full range $\rho \in [0, \infty)$ the solution can be written as

$$u_{k\ell}(\rho) = e^{-\lambda_{k\ell}\rho}\, v_{k\ell}(\rho)$$

for some functions $v_{k\ell}(\rho)$. The solution must behave like a decaying exponential in the limit of large values of ρ, and the hope is that the mathematical side simplifies by singling the exponential out. Note that this does not get rid of the unbound solutions despite the negative sign in the exponent.

By using the chain rule and by eliminating the common factor $e^{-\lambda_{k\ell}\rho}$ the differential equation becomes

$$\left[\lambda_{k\ell}^2 - 2\lambda_{k\ell} \frac{d}{d\rho} + \frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{k\ell}^2 \right] v_{k\ell}(\rho) = 0$$
$$\left[\frac{d^2}{d\rho^2} - 2\lambda_{k\ell} \frac{d}{d\rho} + \frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] v_{k\ell}(\rho) = 0$$

with the boundary condition $v_{k\ell}(0) = 0$ where only the last two steps are shown. The power series with $c_0 \neq 0$

$$v_{k\ell}(\rho) = \rho^s \sum_{q=0}^{\infty} c_q\, \rho^q = \sum_{q=0}^{\infty} c_q\, \rho^{q+s}$$

leads to the two derivatives

$$\begin{aligned}\frac{d}{d\rho}v_{k\ell}(\rho) &= \frac{d}{d\rho}\sum_{q=0}^{\infty}c_q\,\rho^{q+s} = \sum_{q=0}^{\infty}(q+s)c_q\,\rho^{q+s-1}\\ \frac{d^2}{d\rho^2}v_{k\ell}(\rho) &= \frac{d}{d\rho}\sum_{q=0}^{\infty}(q+s)c_q\,\rho^{q+s-1} = \sum_{q=0}^{\infty}(q+s)(q+s-1)c_q\,\rho^{q+s-2}\end{aligned}$$

and the differential equation can be rewritten as

$$\begin{aligned}\sum_{q=0}^{\infty}c_q\left[(q+s)(q+s-1)\rho^{q+s-2} - 2\lambda_{k\ell}(q+s)\rho^{q+s-1} + \left(\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)\rho^{q+s}\right] &= 0\\ \sum_{q=0}^{\infty}c_q\left[\{(q+s)(q+s-1) - \ell(\ell+1)\}\,\rho^{q+s-2} + 2\,\{1-\lambda_{k\ell}(q+s)\}\,\rho^{q+s-1}\right] &= 0\end{aligned}$$

in terms of this power series where

$$\sum_{q=0}^{\infty}c_q\,\rho^{q+s}\bigg|_{\rho=0} \Rightarrow s > 0$$

is required by the boundary condition. This result so far can be summarized as

$$\sum_{q=0}^{\infty}c_q\left[A_q\,\rho^{q+s-2} + B_q\,\rho^{q+s-1}\right] = 0 \qquad\qquad s>0 \qquad\qquad c_0 \neq 0$$

with $A_q = \{(q+s)(q+s-1) - \ell(\ell+1)\}$ and $B_q = 2\,\{1-\lambda_{k\ell}(q+s)\}$. This leads to the set of equations

$$\begin{array}{lll} \rho^{s-2}: & c_0\,A_0 = 0 & \Rightarrow A_0 = s(s-1) - \ell(\ell+1) = 0 \qquad \Rightarrow s = \ell+1\\ \rho^{s-1}: & c_1\,A_1 + c_0\,B_0 = 0 & \\ \vdots & & \\ \rho^{q+s-2}: & c_q\,A_q + c_{q-1}\,B_{q-1} = 0 & \end{array}$$

and to $s = \ell+1$ because $A_0 = 0$ has the two solutions $s = -\ell$ and $s = \ell+1$ but only one is consistent with $s > 0$ and $\ell \geq 0$. The general term with $c_q\,A_q + c_{q-1}\,B_{q-1} = 0$ gives

$$\begin{aligned}&c_q\left[(q+s)(q+s-1) - \ell(\ell+1)\right] + c_{q-1}\cdot 2\left[1-\lambda_{k\ell}(q+s-1)\right] = 0\\ &c_q\left[(q+\ell+1)(q+\ell) - \ell(\ell+1)\right] + 2\,c_{q-1}\left[1-\lambda_{k\ell}(q+\ell)\right] = 0\\ &c_q\,q\big(q+2\ell+1\big) + 2c_{q-1}\big(1-\lambda_{k\ell}(q+\ell)\big) = 0\end{aligned}$$

and the ratio

$$\frac{c_q}{c_{q-1}} = \frac{2(\lambda_{k\ell}(q+\ell)-1)}{q(q+2\ell+1)} \qquad\qquad c_0 \neq 0 \tag{6.10}$$

using $s = \ell+1$.

The function $v_{k\ell}(\rho)$ with the limit

$$v_{k\ell}(\rho) = \sum_{q=0}^{\infty}c_q\,\rho^{q+s}: \qquad\qquad \lim_{q\to\infty}\left\{\frac{c_q}{c_{q-1}}\right\} = \frac{2\,\lambda_{k\ell}\,q}{q^2} = \frac{2\,\lambda_{k\ell}}{q}$$

must be normalizable as an infinite series. The function

$$e^{2\lambda_{k\ell}q} = \sum_{q=0}^{\infty}\frac{(2\lambda_{k\ell})^q}{q!}\rho^q = \sum_{q=0}^{\infty}a_q\rho^q \qquad\qquad a_q = \frac{(2\lambda_{k\ell})^q}{q!} \qquad\qquad \frac{a_q}{a_{q-1}} = \frac{2\lambda_{k\ell}}{q}$$

has the same limit for $q \to \infty$, and comparing

$$v_{k\ell}(\rho) = \sum_{q=0}^{\infty} c_q\, \rho^{q+s} : \qquad \lim_{q\to\infty} \left\{ \frac{c_q}{c_{q-1}} \right\} = \frac{2\,\lambda_{k\ell}}{q}$$

$$e^{2\lambda_{k\ell} q} = \sum_{q=0}^{\infty} a_q \rho^q : \qquad \lim_{q\to\infty} \left\{ \frac{a_q}{a_{q-1}} \right\} = \frac{2\,\lambda_{k\ell}}{q}$$

shows that the difference is just the exponents $q + s$ versus q, and this becomes irrelevant when taking the limit $q \to \infty$. This means that $v_{k\ell}(\rho) \sim e^{2\lambda_{k\ell} q}$ for high-order terms in the expansion if the series is infinite. However, this is a problem because the exponent $2\,\lambda_{k\ell}\, q$ is positive and the exponential function becomes increasingly large for large values ρ. Thus, the physically relevant solutions for $v_{k\ell}(\rho)$ must correspond to power series with a finite number of terms.

Therefore, there must be a $q = k$ such that $c_k = 0$ and it follows from (6.10) that $c_q = 0$ for all $q \geq k$. It follows further

$$\lambda_{k\ell}(k+\ell) - 1 = 0 \qquad \lambda_{k\ell} = \sqrt{-\frac{E_{k\ell}}{E_{\mathrm{I}}}} = \frac{1}{k+\ell} \qquad E_{k\ell} = -E_{\mathrm{I}}\, \lambda_{k\ell}^2 = -\frac{E_{\mathrm{I}}}{(k+\ell)^2}$$

and thus also $k = 1, 2, 3, 4, ...$ because of $\ell = 0, 1, 2, 3, ...$ and $c_0 \neq 0$. This also means that the energy eigenvalues of the bound states of the hydrogen atom

$$E_{k\ell} = -\frac{E_{\mathrm{I}}}{(k+\ell)^2} \qquad \ell = 0, 1, 2, 3, ... \qquad k = 1, 2, 3, 4, ... \tag{6.11}$$

are quantized.

Inserting this result into the ratio (6.10) gives iteratively

$$\begin{aligned}
c_q &= \frac{2(k-q)}{q(q+2\ell+1)(k+\ell)} c_{q-1} \text{ from } \frac{c_q}{c_{q-1}} = \frac{2\left(\frac{q+\ell}{k+\ell} - 1\right)}{q(q+2\ell+1)} = \frac{2(k-q)}{q(q+2\ell+1)(k+\ell)} \\
&= (-1)^2 \left(\frac{2}{k+\ell}\right)^2 \frac{(k-q)(k-q+1)}{q(q-1)(q+2\ell+1)(q+2\ell)}\, c_{q-2} \\
&= (-1)^q \left(\frac{2}{k+\ell}\right)^q \frac{(k-q)(k-q+1)\ldots(k-1)}{q(q-1)\ldots 1(q+2\ell+1)(q+2\ell)\ldots(2\ell+2)}\, c_0 \\
&= (-1)^q \left(\frac{2}{k+\ell}\right)^q \frac{(k-1)!/(k-q-1)!}{q!\,(q+2\ell+1)!/(2\ell+1)!}\, c_0 = (-1)^q \left(\frac{2}{k+\ell}\right)^q \frac{(k-1)!}{(k-q-1)!} \frac{(2\ell+1)!}{q!\,(q+2\ell+1)!}\, c_0
\end{aligned}$$

for the coefficient c_q expressed in terms of c_0. Finally, c_0 has to be determined through normalization, and the radial eigenfunctions $R_{k\ell}$ can be determined from $u_{k\ell}$ and $v_{k\ell}$.

6.4 The Quantum Virial Theorem

The virial theorem encodes a simple relation between kinetic and potential energy of any quantum system. It holds even for quantum systems where no exact solution is available

A time independent Hamiltonian with the eigenvalue equation $\hat{H}\,|\psi_n\rangle = E_n\,|\psi_n\rangle$ has the dual eigenvalue equation $\langle\psi_n|\,\hat{H} = E_n\,\langle\psi_n|$ because the Hamiltonian is a Hermitian operator and the eigenvalue is real such that no adjoint and complex conjugate is needed. For a time independent operator $\hat{A}$ the expectation value of the commutator of the Hamitonian and $\hat{A}$ is therefore

$$\begin{aligned}
\langle\psi_n|\,[\hat{H},\hat{A}]\,|\psi_n\rangle = \langle\psi_n|\hat{H}\hat{A} - \hat{A}\hat{H}|\psi_n\rangle &= \underbrace{\langle\psi_n|\hat{H}}_{E_n\,\langle\psi_n|}\hat{A}|\psi_n\rangle - \langle\psi_n|\hat{A}\underbrace{\hat{H}|\psi_n\rangle}_{E_n\,|\psi_n\rangle} \\
&= E_n\,\langle\psi_n|\hat{A}|\psi_n\rangle - E_n\,\langle\psi_n|\hat{A}|\psi_n\rangle = 0
\end{aligned}$$

with respect to an eigenstate of the system. This result is called the *hypervirial theorem.*

The Hamiltonian of a single particle moving in one direction is

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = \hat{T} + \hat{V}$$

where the kinetic energy operator is called $\hat{T}$ and the potential energy operator is called $\hat{V}$ without specifying the dependence on the position operator $\hat{x}$. Selecting $\hat{A} = \hat{x}\hat{p}$ the commutator in the hypervirial theorem becomes $[\hat{H}, \hat{x}\hat{p}] = \hat{x}[\hat{H}, \hat{p}] + [\hat{H}, \hat{x}]\hat{p}$ using $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$. With

$$\begin{aligned}
[\hat{H}, \hat{p}] &= \left[\frac{\hat{p}^2}{2m}, \hat{p}\right] + [V(\hat{x}, \hat{p}] = 0 + i\hbar V'(\hat{x}) = i\hbar V'(\hat{x}) \\
[\hat{H}, \hat{x}] &= \left[\frac{\hat{p}^2}{2m}, \hat{x}\right] + [V(\hat{x}, \hat{x}] = \frac{1}{2m}\big(\hat{p}[\hat{p}, \hat{x}] + [\hat{p}, \hat{x}]\hat{p}\big) + 0 = -\frac{i\hbar}{m}\hat{p}
\end{aligned}$$

the commutator $[\hat{H}, \hat{x}\hat{p}]$ becomes

$$[\hat{H}, \hat{x}\hat{p}] = \hat{x}[\hat{H}, \hat{p}] + [\hat{H}, \hat{x}]\hat{p} = i\hbar\hat{x}V'(\hat{x}) - \frac{i\hbar}{m}\hat{p}^2 = i\hbar\left(\hat{x}V'(\hat{x}) - 2\left(\frac{\hat{p}^2}{2m}\right)\right) = i\hbar\left(\hat{x}V'(\hat{x}) - 2\hat{T}\right)$$

in compact form. This gives

$$i\hbar\,\langle\psi_n|\hat{x}V'(\hat{x})|\psi_n\rangle - 2i\hbar\,\langle\psi_n|\hat{T}|\psi_n\rangle = 0$$

using the hypervirial theorem and leads to the *virial theorem*

$$\langle\psi_n|\hat{x}V'(\hat{x})|\psi_n\rangle = 2\,\langle\psi_n|\hat{T}|\psi_n\rangle \tag{6.12}$$

where $|\psi_n\rangle$ is an energy eigenstate. This is usually written as $\langle\hat{x}V'(\hat{x})\rangle = 2\,\langle\hat{T}\rangle$ where one has to remember that these expectation values are calculated with respect to the energy eigenstates of the system.

The virial theorem provides a very general relationship between the expectation values of potential and kinetic energies without the need to explicitly evaluate them. Calculations of expectation values can be tedious because they may require the evaluation of long integrals. Most quantum systems cannot be solved analytically such that one has to work with approximate solutions.

There is also a virial theorem in the form $2\,\langle T\rangle = \langle x\frac{dV}{dx}\rangle = -\,\langle xF\rangle$ in classical mechanics using the fact that the derivative of the potential energy is the negative force. (This is the reason for the name of the virial theorem because the Latin word for force is vis.) Here the expectation value in quantum mechanics corresponds to the time average.

The virial theorem takes a rather simple form for the special class of potentials described by homogeneous functions of degree k. These functions have the property $f(s\,x) = s^k\,f(x)$ where $s \neq 0$ is a scalar. An example is $f(x) = \lambda x^2$ because $f(s\,x) = \lambda(s\,x)^2 = s^2(\lambda x^2) = s^2 f(x)$. Due to Euler's theorem

$$f(s\,x) = s^k\,f(x) \qquad\qquad \Rightarrow \qquad\qquad k\,f(x) = x\frac{df}{dx}$$

following from

$$\left.\begin{aligned}
&\frac{df}{ds}f(s\,x) = \frac{df}{d(sx)}\frac{d(sx)}{ds} = x\frac{df}{d(sx)} \\
&\frac{d}{ds}\big(s^k\,f(x)\big) = k\,s^{k-1}f(x)
\end{aligned}\right\} \qquad\qquad x\frac{df}{d(sx)} = k\,s^{k-1}f(x)$$

for the case $s = 1$. If the potential energy is described by a homogeneous function obeying therefore $V(s\,\hat{x}) = s^k\,V(\hat{x})$ then $k\,V(\hat{x}) = \hat{x}\,V'(\hat{x})$ according to Euler's theorem. Inserting this into the virial theorem gives

$$k\,\langle\hat{V}\rangle = 2\,\langle\hat{T}\rangle \tag{6.13}$$

for homogeneous potentials. Because of $\langle\hat{H}\rangle = \langle\psi_n|\hat{H}|\psi_n\rangle = E_n = \langle\hat{T}\rangle + \langle\hat{V}\rangle$ either $\langle\hat{T}\rangle$ can be expressed in terms of $\langle\hat{V}\rangle$ or vice versa using (6.13). The result is

$$\langle\hat{T}\rangle = \frac{k\,E_n}{k+2} \qquad\qquad \langle\hat{V}\rangle = \frac{2\,E_n}{k+2}$$

and there are many potential that are described by homogeneous functions. Two important examples are the quantum harmonic oscillator and the hydrogen atom.

The quantum harmonic oscillator has the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

where the potential is a homogeneous function with $k = 2$. Therefore, the relation

$$\langle \hat{V} \rangle = \langle \hat{T} \rangle$$

follows from the virial theorem (6.13) without the need for an analytical solution of the harmonic oscillator. There is an analytical solution for the harmonic oscillator such that this equality can be checked but there are many quantum problems where there is none and where the virial theorem is extremely useful.

Although the discussion so far has been limited to a single particle moving in one dimension, the virial theorem can be generalized to systems with multiple particles in three dimensions. Given a system of N particles with position $\underline{\hat{r}}_i = (\hat{x}_i, \hat{y}_i, \hat{z}_i)$, momenta $\underline{\hat{p}}_i = (\hat{p}_{xi}, \hat{p}_{yi}, \hat{p}_{zi})$ and masses m_i for $i = 1, 2, ..., N$ the Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \frac{\underline{\hat{p}}_i^2}{2m_i} + V(\underline{\hat{r}}_1, \underline{\hat{r}}_2, ..., \underline{\hat{r}}_N) = \hat{T} + \hat{V}$$

can be split similarly to the case in one dimension into $\hat{T}$ and $\hat{V}$ where $\hat{T}$ is the sum of all kinetic terms and $\hat{V}$ is the potential $V(\underline{\hat{r}}_1, \underline{\hat{r}}_2, ..., \underline{\hat{r}}_N)$. The virial theorem becomes

$$\left\langle \sum_{i=1}^{N} \underline{\hat{r}}_i \cdot \nabla_i V(\underline{\hat{r}}_1, \underline{\hat{r}}_2, ..., \underline{\hat{r}}_N) \right\rangle = 2 \langle \hat{T} \rangle \tag{6.14}$$

in this generalized case.

Also here play homogeneous functions an important role. Homogeneous functions of degree k with n variables have the property $f(s\,x_1, s\,x_2, ..., s\,x_n) = s^k f(x_1, x_2, ..., x_n)$ where $s \neq 0$ is a scalar. Euler's theorem becomes

$$k\, f(x_1, x_2, ..., x_n) = \sum_{i=1}^{n} x_i \frac{\partial f}{\partial x_i}$$

and

$$k \langle \hat{V} \rangle = 2 \langle \hat{T} \rangle \tag{6.15}$$

is the virial theorem for a system with multiple particles in three dimensions with a homogeneous function as the potential.

The potential energy of the hydrogen atom is given by the electrostatic interaction $V(\underline{\hat{r}}_p, \underline{\hat{r}}_e)$ between a proton and an electron and can be written in the form

$$V(\hat{x}_p, \hat{y}_p, \hat{z}_p, \hat{x}_e, \hat{y}_e, \hat{z}_e) = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{\left[(\hat{x}_p - \hat{x}_e)^2 + (\hat{y}_p - \hat{y}_e)^2 + (\hat{z}_p - \hat{z}_e)^2\right]^{1/2}}$$

in terms of six variables. This is a homogeneous function $V(s\,\underline{\hat{r}}_p, s\,\underline{\hat{r}}_e) = s^{-1} V(\underline{\hat{r}}_p, \underline{\hat{r}}_e)$ with $k = -1$ such that $\langle \hat{V} \rangle = -2 \langle \hat{T} \rangle$ according to (6.15). For any atom, molecule, or other material the potential energy of a two-body system always has the form of the electrostatic interaction

$$V(\underline{\hat{r}}_1, \underline{\hat{r}}_2) = \frac{1}{4\pi\varepsilon_0} \frac{q_1\, q_2}{|\underline{\hat{r}}_1 - \underline{\hat{r}}_2|}$$

between any two particles irrespective of how complex the system is. (The quantity $q_1\, q_2$ is the product of the two charges.) The two-body interaction obeys the relation $V(s\,\underline{\hat{r}}_1, s\,\underline{\hat{r}}_2) = s^{-1} V(\underline{\hat{r}}_1, \underline{\hat{r}}_2)$ such that the virial theorem (6.15) leads to $\langle \hat{V} \rangle = -2 \langle \hat{T} \rangle$ as for the hydrogen atom. This is a very general result because most quantum systems with multiple particles other than the hydrogen atom does not have an analytical solution.

6.5 Eigenvalues and Eigenfunctions of the Hydrogen Atom

The relative motion of the hydrogen atom consisting of a proton and an electron is

$$\hat{H}_{\text{rel}} = \frac{\hat{\underline{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\hat{\underline{r}}|} \qquad \frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \qquad \hat{\underline{p}} = \frac{m_e\hat{\underline{p}}_p - m_p\hat{\underline{p}}_e}{m_p + m_e} \qquad \hat{\underline{r}} = \hat{\underline{r}}_p - \hat{\underline{r}}_e$$

according to (6.8). The relative Hamiltonian is

$$\hat{H}_{\text{rel}} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

in position representation where the potential is a central potential. (In the following $\hat{H}$ is used instead of $\hat{H}_{\text{rel}}$ to simplify notation.) The eigenvalue equation for the Hamiltonian is

$$\hat{H}\psi(\underline{r}) = E\psi(\underline{r}) \qquad \hat{\underline{L}}^2\,\psi(\underline{r}) = \ell(\ell+1)\hbar^2\,\psi(\underline{r}) \qquad \hat{L}_z\,\psi(\underline{r}) = m_\ell\hbar\,\psi(\underline{r})$$

together with the eigenvalue equations for $\hat{\underline{L}}^2$ and $\hat{L}_z$ where the possible values for ℓ and m_ℓ are $\ell = 0, 1, 2, ...$ and $m_\ell = -\ell, -\ell+1, ..., \ell-1, \ell$. The eigenvalue equation for the Hamiltonian becomes

$$\hat{H}\,\psi_{k\ell m_\ell}(\underline{r}) = E_{k\ell}\,\psi_{k\ell m_\ell}(\underline{r}) \tag{6.16}$$

where the eigenfunctions and eigenvalues are labeled with the appropriate quantum numbers. For every combination of the orbital quantum numbers ℓ and m_ℓ there is a spectrum of energy eigenfunctions labeled by the additional quantum number k. The energy eigenvalues $E_{k\ell}$ do not depend on m_ℓ as can be shown for any central potential. The eigenfunction $\psi_{k\ell m_\ell}(\underline{r})$ is given as a product of a radial part and an angular part

$$\psi_{k\ell m_\ell}(\underline{r}) = R_{k\ell}(r)\,Y_\ell^{m_\ell}(\vartheta, \varphi) \tag{6.17}$$

where the angular functions are the spherical harmonics applicable to any central potential and the radial functions depend on the form of the radial potential.

The development of the radial functions follows the path

$$\begin{aligned}
&R_{k\ell}(r) = \frac{1}{r}u_{k\ell}(r) && && \\
&u_{k\ell}(r) \to u_{k\ell}(\rho) && \rho = \frac{r}{a_0} && a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \\
&u_{k\ell}(\rho) = e^{-\lambda_{k\ell}\rho}v_{k\ell}(\rho) && \lambda_{k\ell} = \sqrt{-\frac{E_{k\ell}}{E_{\text{I}}}} && E_{\text{I}} = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \\
&v_{k\ell}(\rho) = \sum_{q=0}^{\infty} c_q\rho^{q+s} && s = \ell + 1 &&
\end{aligned}$$

with

$$c_q = \begin{cases} (-1)^q \left(\dfrac{2}{k+\ell}\right)^q \dfrac{(k-1)!}{(k-q-1)!}\,\dfrac{(2\ell+1)!}{q!\,(q+2\ell+1)!}\,c_0 & \text{if } q < k \\ 0 & \text{if } q \geq k \end{cases} \tag{6.18}$$

started in the discussion of the power series solution for the hydrogen atom. Here the functions $R_{k\ell}(r)$ are determined completely. The topic is the non-relativistic hydrogen atom leaving things such as spin, fine structure or hyperfine structure aside.

In a first step c_0 has to be determined by normalization

$$\int d\underline{r}\,|\psi_{k\ell m_\ell}(\underline{r})|^2 = 1$$

but the radial and the angular part can be normalized separately

$$\int_0^\infty r^2 dr\,|R_{k\ell}(r)|^2 = 1 \qquad\qquad \int_0^\pi \sin\vartheta\,d\vartheta \int_0^{2\pi} d\varphi\,|Y_\ell^m(\vartheta,\varphi)|^2 = 1$$

as can be shown for any central potential. The spherical harmonics are already normalized. In order to normalize the radial function the simpler integral

$$\int_0^\infty dr\,|u_{k\ell}(r)|^2 = 1$$

can be used.

The energy eigenvalues are negative for bound states and the formula for them

$$E_{k\ell} = -\frac{E_\mathrm{I}}{(k+\ell)^2} \qquad \to \qquad E_n = -\frac{E_\mathrm{I}}{n^2} = -\frac{\mu e^4}{32\pi^2\,\varepsilon_0^2\,\hbar^2\,n^2}$$

according to (6.11) can be simplified by introducing $n = k+\ell$. Because of $\ell = 0, 1, 2, \ldots$ and $k = 1, 2, 3, \ldots$ the values for n must be positive integer values. In the ground state $n = 1$ there is only one possibility $k = 1$ and $\ell = 0$, but for the first excited state $n = 2$ there are two possibilities $k = 2$ and $\ell = 0$ or $k = 1$ and $\ell = 1$. This means that one can either label the eigenfunctions $\psi_{k\ell m_\ell}(\underline{r})$ with the quantum number k or $\psi_{n\ell m_\ell}(\underline{r})$ with the quantum number n. The second option is the most common.

The ground state energy E_1 is minus the ionization energy E_I and can therefore be written as

$$E_1 = -\frac{\mu e^4}{32\pi^2\,\varepsilon_0^2\,\hbar^2}$$

explicitly. The eigenfunction of the ground state has a single term c_0 in the power series expansion according to (6.18). Thus, $v_{10} = c_0\,\rho$ because $k = 1$ and $\ell = 0$. Going back in the various substitution steps gives

$$u_{10}(\rho) = c_0\,\rho\,e^{-\lambda_{10}\rho} = c_0\,\rho\,e^{-\rho} \qquad\qquad u_{10}(r) = c_0\frac{r}{a_0}e^{-r/a_0}$$

because $\lambda_{10} = 1$. The result for normalization becomes

$$1 = \int_0^\infty dr\,|u_{k\ell}(r)|^2 = \frac{|c_0|^2}{a_0^2}\int_0^\infty dr\,r^2\,e^{-2r/a_0} = \frac{|c_0|^2}{a_0^2}\frac{2!}{(2/a_0)^3} = |c_0|^2\,\frac{a_0}{4} \qquad\Rightarrow\qquad c_0 = \frac{2}{\sqrt{a_0}}$$

using

$$\int_0^\infty dx\,x^p\,e^{-\alpha x} = \frac{p!}{\alpha^{p+1}}$$

with $p = 2$ and $\alpha = 2/a_0$. Thus, the ground state eigenfunction is

$$u_{10}(r) = \frac{2}{\sqrt{a_0^3}}r\,e^{-r/a_0} \qquad\Rightarrow\qquad R_{10}(r) = \frac{2}{\sqrt{a_0^3}}e^{-r/a_0} \qquad\Rightarrow\qquad \psi_{100}(\underline{r}) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

and has the quantum numbers $k = 1$, $\ell = 0$, $m_\ell = 0$ or, equally, the quantum numbers $n = 1$, $\ell = 0$, $m_\ell = 0$.

The first excited state with $n = 2$ has the eigenvalue $E_2 = -E_\mathrm{I}/4$ and the two possibilities $k = 2$, $\ell = 0$ or $k = 1$ and $\ell = 1$. The power series solution for $k = 2$, $\ell = 0$ has the two non-zero coefficients c_0 and $c_1 = -c_0/2$ using (6.18). This gives

$$v_{20}(\rho) = c_0\,\rho + c_1\,\rho^2 = c_0\left(\rho - \frac{1}{2}\rho^2\right) \quad u_{20}(\rho) = c_0\left(\rho - \frac{1}{2}\rho^2\right)e^{-\rho/2} \quad u_{20}(r) = c_0\left(\frac{r}{a_0} - \frac{r^2}{2a_0^2}\right)e^{-r/2a_0}$$

with the normalization

$$1 = \int_0^\infty dr\,|u_{20}(r)|^2 = |c_0|^2\int_0^\infty dr\left(\frac{r^2}{a_0^2}e^{-r/a_0} - \frac{r^3}{a_0^3}e^{-r/a_0} + \frac{r^4}{4a_0^4}e^{-r/a_0}\right) = 2a_0|c_0|^2 \quad\Rightarrow\quad c_0 = \frac{1}{\sqrt{2a_0}}$$

using the same integral as above to determine c_0. The result for this case is

$$u_{20}(r) = \frac{1}{\sqrt{2a_0}}\left(\frac{r}{a_0} - \frac{r^2}{2a_0^2}\right) e^{-r/2a_0} \qquad\qquad R_{20}(r) = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

and the full eigenfunction becomes

$$\psi_{200}(\underline{r}) = \frac{1}{\sqrt{8\pi a_0^3}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

for the (k,ℓ,m_ℓ) and the (n,ℓ,m_ℓ) notation.

The power series solution for $k = 1$, $\ell = 1$ for the first excited state, on the other hand, has only one non-zero coefficient c_0. Thus, one gets

$$v_{11}(\rho) = c_0\,\rho^2 \qquad\qquad u_{11}(\rho) = c_0\,\rho^2 e^{-\rho/2} \qquad\qquad u_{11}(r) = c_0\,\frac{r^2}{a_0^2} e^{-r/2a_0}$$

and normalization gives c_0 through

$$1 = \int_0^\infty dr\,|u_{11}(r)|^2 = \frac{|c_0|^2}{a_0^4}\int_0^\infty dr\, r^4\, e^{-r/a_0} = 24a_0|c_0|^2 \qquad \Rightarrow \qquad c_0 = \frac{1}{\sqrt{24a_0}}$$

again with the same general integral. Undoing the substitutions gives

$$u_{11}(r) = \frac{1}{\sqrt{24a_0}}\frac{r^2}{a_0^2} e^{-r/2a_0} \qquad\qquad R_{11}(r) = \frac{1}{\sqrt{24a_0^3}}\frac{r}{a_0} e^{-r/2a_0}$$

and the three possible eigenfunction in (k,ℓ,m_ℓ) notation become

$$\begin{aligned}
\psi_{11-1}(\underline{r}) &= \frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, e^{-i\varphi}\sin\vartheta \\
\psi_{110}(\underline{r}) &= \frac{1}{4\sqrt{2\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, \cos\vartheta \\
\psi_{111}(\underline{r}) &= -\frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, e^{i\varphi}\sin\vartheta
\end{aligned}$$

because $m_\ell = -1, 0, 1$ for $\ell = 1$. In the (n,ℓ,m_ℓ) notation they are labeled as $\psi_{21-1}(\underline{r})$, $\psi_{210}(\underline{r})$, $\psi_{211}(\underline{r})$.

To summarize, the ground state with $E_1 = -E_{\mathrm{I}}$ and the first excited state with $E_2 = -E_{\mathrm{I}}/4$ have

$$\begin{aligned}
(1,0,0): &\quad \psi_{100}(\underline{r}) = R_{10}(r)\cdot Y_0^0(\vartheta,\varphi) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}\cdot\frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \\
(2,0,0): &\quad \psi_{200}(\underline{r}) = R_{20}(r)\cdot Y_0^0(\vartheta,\varphi) = \frac{1}{\sqrt{8\pi a_0^3}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \\
(2,1,-1): &\quad \psi_{21-1}(\underline{r}) = R_{21}(r)\cdot Y_1^{-1}(\vartheta,\varphi) = \frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, e^{-i\varphi}\sin\vartheta \\
(2,1,0): &\quad \psi_{210}(\underline{r}) = R_{21}(r)\cdot Y_1^0(\vartheta,\varphi) = \frac{1}{4\sqrt{2\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, \cos\vartheta \\
(2,1,1): &\quad \psi_{211}(\underline{r}) = R_{21}(r)\cdot Y_1^1(\vartheta,\varphi) = -\frac{1}{8\sqrt{\pi a_0^3}}\frac{r}{a_0} e^{-r/2a_0}\, e^{i\varphi}\sin\vartheta
\end{aligned} \tag{6.19}$$

in the (n,ℓ,m_ℓ) notation. The next excited state with eigenvalue $E_3 = -E_{\mathrm{I}}/9$ has the nine eigenfunctions

$n = 3, \ell = 0:$ $\psi_{300}(\underline{r})$
$n = 3, \ell = 1:$ $\psi_{31-1}(\underline{r}), \psi_{310}(\underline{r}), \psi_{311}(\underline{r})$
$n = 3, \ell = 2:$ $\psi_{32-2}(\underline{r}), \psi_{32-1}(\underline{r}), \psi_{320}(\underline{r}), \psi_{321}(\underline{r}), \psi_{322}(\underline{r})$

without the explicit functions. The radial parts of the eigenfunctions for the ground state and the first excited state are shown in figure 1. The graph of $R_{10}(r)$ for the ground state is given in (a), and the graphs of $R_{20}(r)$ and $R_{21}(r)$ for the first excited state in (b) and (c), respectively. The first excited state is fourfold degenerate, and the second excited state is ninefold degenerate.

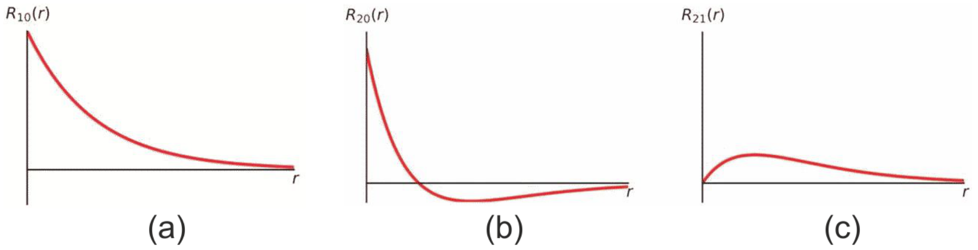


Figure 1: The radial part of the eigenfunctions $R_{10}(r)$, $R_{20}(r)$ and $R_{21}(r)$

6.6 Groundstate of the Hydrogen Atom

The relative Hamiltonian according to (6.8) is

$$\hat{H} = \frac{\hat{\underline{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\hat{\underline{r}}|} \qquad\qquad \hat{H}\,\psi_{k\ell m_\ell}(\underline{r}) = E_m\,\psi_{k\ell m_\ell}(\underline{r})$$

with its eigenvalue equation. In order to determine the ground state energy, the energy eigenvalue can be expressed as

$$E_n = -\frac{E_{\mathrm{I}}}{n^2} \qquad\qquad E_{\mathrm{I}} = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

in terms of the ionization energy (6.9). This gives

$$E_1 = -E_{\mathrm{I}} = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

for the ground state energy. The reduced mass μ is

$$\mu = \frac{m_p\,m_e}{m_p + m_e} = 9.104\cdot 10^{-31}\,\mathrm{kg} \qquad m_p = 1.673\cdot 10^{-27}\,\mathrm{kg} \qquad m_e = 9.109\cdot 10^{-31}\,\mathrm{kg}$$

where m_p is the proton mass and m_e the electron mass, and the ground state energy becomes

$$E_1 = -E_{\mathrm{I}} = -2.176\cdot 10^{-18}\,\mathrm{J} = -13.6\,\mathrm{eV} \qquad e = 1.602\cdot 10^{-19}\,\mathrm{C} \qquad \varepsilon_0 = 8.854\cdot 10^{-12}\,\mathrm{m}^{-3}\,\mathrm{kg}^{-1}\,\mathrm{s}^4\,\mathrm{A}^2$$

given e, ε_0, $\hbar = 1.055\cdot 10^{-34}\,\mathrm{J\,s}$ and $1\,\mathrm{eV} = 1.602\cdot 10^{-19}\,\mathrm{J}$. The negative sign shows that this is a bound state. Thus, the energy $E_{\mathrm{I}} = 13.6\,\mathrm{eV}$ is needed to unbind the electron from the hydrogen atom in its ground state, and this is called the ionization energy.

The ground state wave function is

$$\psi_{n\ell m_\ell}(\underline{r}) = R_{n\ell}(r)\,Y_\ell^{m_\ell}(\vartheta,\varphi)$$

according to (6.17) for $n = 1, \ell = 0, m_\ell = 0$ where the functions $Y_\ell^{m_\ell}$ are the spherical harmonics and the functions $R_{n\ell}$ are called the radial part. This gives

$$\psi_{100}(\underline{r}) = R_{10}(r)\cdot Y_0^0(\vartheta,\varphi) = \frac{2}{\sqrt{a_0^3}}e^{-r/a_0}\cdot\frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

as shown in (6.19). The radial part is depicted in figure 1 (a), and $Y_0^0(\vartheta,\varphi)$ is simply a constant. Thus, the ground state wave function of the hydrogen atom takes its maximal value at the origin of the potential and then decays away from the origin in an isotropic manner.

The next question is what is the probability $P(\underline{r})\,d\underline{r}$ of finding the electron around $\underline{r}$ within the volume element $d\underline{r}$. This probability is

$$P(\underline{r})\,d\underline{r} = |\psi_{100}(\underline{r})|^2\,d\underline{r} = |R_{10}(r)|^2\left|Y_0^0(\vartheta,\varphi)\right|^2 d\underline{r} = \frac{1}{\pi a_0^3}e^{-2r/a_0}\,d\underline{r} = \frac{1}{\pi a_0^3}e^{-2r/a_0}\,r^2\,dr\,\sin(\vartheta)\,d\vartheta\,d\varphi$$

using $d\underline{r} = r^2\, dr\, \sin(\vartheta)\, d\vartheta\, d\varphi$ in spherical coordinates. Because the ground state wave function is isotropic one can ignore the angular part and only look at the radial part by asking what the probability $p(r)\, dr$ is of finding the electron in the interval $(r, r + dr)$. It is

$$p(r)\, dr = \left|R_{10}(r)\right|^2 r^2\, dr \int_0^{\pi} \sin(\vartheta)\, d\vartheta \int_0^{2\pi} \left|Y_0^0(\vartheta,\varphi)\right|^2 d\varphi = \left|R_{10}(r)\right|^2 r^2\, dr$$

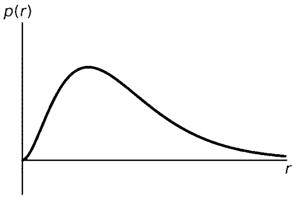
because

$$\int_0^{\pi} \sin(\vartheta)\, d\vartheta \int_0^{2\pi} \left|Y_0^0(\vartheta,\varphi)\right|^2 d\varphi = \frac{1}{4\pi} \int_0^{\pi} \sin(\vartheta)\, d\vartheta \int_0^{2\pi} d\varphi = 1$$

for the angular part. Inserting $R_{10}(r)$ gives

$$p(r) = \left|R_{10}(r)\right|^2 r^2 = \frac{4}{a_0^3}\, r^2\, e^{-2r/a_0}$$

for the probability density $p(r)$.



The graph on the right side shows the probability density $p(r)$ for the ground state. Compared to the radial part of the wave function of the ground state shown in figure 1 (a), it does not have the maximum at the origin but some distance away from the origin due to the term r^2. In order to determine the position of the maximum, the derivative $dp(r)/dr$ can be set to zero giving

$$\frac{d}{dr}\left(\frac{4}{a_0^3}\, r^2\, e^{-2r/a_0}\right) = \frac{8}{a_0^3}\, e^{-2r/a_0}\left(1 - \frac{r}{a_0}\right) = 0 \qquad \Rightarrow \qquad r = a_0$$

such that the most likely distance of the electron from the proton is the reduced Bohr radius a_0 introduced in (6.9). It therefore describes the typical size of the hydrogen atom. The numerical value of the reduced Bohr radius is $a_0 = 5.3 \cdot 10^{-11}$ m $= 0.53$ Å calculated using the values for μ, e, ε_0 and $\hbar$ presented above.

As a last property of the hydrogen atom the separated contributions of the kinetic and the potential energy to the energy of the ground state are calculated. The relative Hamiltonian from (6.8) can be written as $\hat{H} = \hat{T} + \hat{V}$. This means

$$\left.\begin{array}{l} \langle \hat{H} \rangle = \langle \psi_{100} | \hat{H} | \psi_{100} \rangle = \langle \psi_{100} | E_1 | \psi_{100} \rangle = E_1 = -E_{\mathrm{I}} \\ \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle \end{array}\right\} \Rightarrow \langle \hat{T} \rangle + \langle \hat{V} \rangle = -E_{\mathrm{I}}$$

in terms of the expectation values. The expectation value $\langle \hat{V} \rangle$ is

$$\langle \hat{V} \rangle = \left\langle \psi_{100} \left| -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\hat{\underline{r}}|} \right| \psi_{100} \right\rangle = -\frac{e^2}{4\pi\varepsilon_0} \left\langle \psi_{100} \left| \frac{1}{|\hat{\underline{r}}|} \right| \psi_{100} \right\rangle = -\frac{e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{|\hat{\underline{r}}|} \right\rangle = -\frac{e^2}{4\pi\, \varepsilon_0\, a_0}$$

using

$$\left\langle \frac{1}{|\hat{\underline{r}}|} \right\rangle = \int_0^{\pi} \sin(\vartheta)\, d\vartheta \int_0^{2\pi} d\varphi \int_0^{\infty} r^2\, dr\, |\psi_{100}(\underline{r})|^2) = \frac{4\pi}{\pi a_0^3} \frac{1!}{\left(\frac{2}{a_0}\right)^2} = \frac{1}{a_0} \qquad \int_0^{\infty} dx\, x^p\, e^{-\alpha x} = \frac{p!}{\alpha^{p+1}}$$

and $\psi_{100}(\underline{r})$ from (6.19). Rearranging E_{I} using a_0 both from (6.9)

$$E_{\mathrm{I}} = \frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = \frac{e^2}{8\pi\, \varepsilon_0}\left(\frac{\mu\, e^2}{4\pi\, \varepsilon_0\, \hbar^2}\right) = \frac{e^2}{8\pi\, \varepsilon_0} a_0^{-1} = \frac{e^2}{8\pi\, \varepsilon_0\, a_0}) = -\frac{1}{2} \langle \hat{V} \rangle$$

shows that $\langle \hat{V} \rangle = -2\, E_{\mathrm{I}}$. This leads to $\langle \hat{T} \rangle = \langle \hat{H} \rangle - \langle \hat{V} \rangle = -E_{\mathrm{I}} - (-2\, E_{\mathrm{I}}) = E_{\mathrm{I}}$ Thus, the magnitude of the potential energy contribution to the total energy is twice as large as the contribution from the kinetic energy for the ground state of the hydrogen atom because $\langle \hat{V} \rangle = -2\, \langle \hat{T} \rangle$. This is an example of the quantum virial theorem introduced above. This result is not only valid for the ground state of the hydrogen atom but also for any excited state.

6.7 Energy Spectrum of the Hydrogen Atom

The relative Hamiltonian of the hydrogen atom is

$$\hat{H} = \frac{\underline{\hat{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\underline{\hat{r}}|} \qquad\qquad \hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

in momentum representation (6.8) and in position representation with $\hat{H}\,\psi_{k\ell m_\ell}(\underline{r}) = E_{k\ell}\,\psi_{k\ell m_\ell}(\underline{r})$ as the energy eigenvalue equation (6.16). The quantum numbers are $k = 1, 2, 3, ...$ which is directly associated with the Hamiltonian eigenvalues and $\ell = 0, 1, 2, ...$ as well as $m_\ell = -\ell, -\ell + 1, ..., \ell - 1, \ell$ which are associated with the angular momentum. Because $E_{k\ell}$ is independent of m_ℓ it is at least $(2\ell + 1)$-fold degenerate. The degeneracy $g_\ell = 2\ell + 1$ is a direct consequence of the rotational invariance.

There are more degeneracies because the values $E_{k\ell}$ only depend on the sum $k + \ell$ according to (6.11) such that $E_{k_1\ell_1} = E_{k_2\ell_2}$ for $k_1 + \ell_1 = k_2 + \ell_2$. Classically this symmetry is present in any potential that arises from an inverse square law such as Coulomb's law of electrostatics and Newton's law of gravity. All these potentials conserve what is called the Runge-Lenz vector. There is a corresponding quantity in quantum mechanics that leads to this additional symmetry. Introducing a new label n as above gives

$$E_{k\ell} = \frac{E_{\mathrm{I}}}{(k+\ell)^2} \qquad \overset{n=k+\ell}{\Longrightarrow} \qquad E_n = \frac{E_{\mathrm{I}}}{n^2}$$

where $n = 1, 2, 3, ...$ because $k = 1, 2, 3, ...$ and $\ell = 0, 1, 2, ...$ For a given n the quantum number ℓ can take values $\ell = 0, 1, ..., n - 1$, and

$$\hat{H}\,\psi_{n\ell m_\ell} = E_n\,\psi_{n\ell m_\ell}$$

is the corresponding energy eigenvalue equation.

The degeneracy of E_n is of $g_\ell = 2\ell + 1$ for each possible value of m_ℓ giving

$$g_n = \sum_{\ell=0}^{n-1} g_\ell = \sum_{\ell=0}^{n-1}(2\ell + 1) = n^2$$

because ℓ can take any of the n values $0, ..., n - 1$. Taking spin into account then the degeneracy doubles. (Note that this is the non-relativistic hydrogen atom.)

Since the three quantum numbers (n, ℓ, m_ℓ) are important they have been named. The quantum number n is called principal quantum number, ℓ is called azimuthal quantum number, and m_ℓ is called magnetic quantum number. The last name comes from the fact the energy eigenvalues are degenerate in m_ℓ unless there is a magnetic field.

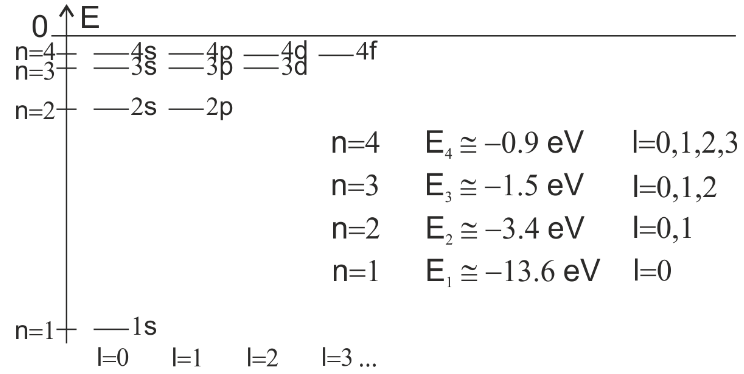


Figure 2: The first four energy eigenvalues of the hydrogen atom

The first four energy eigenvalues of the hydrogen atom are shown in figure 2 with the principal quantum number n and the possible azimuthal quantum numbers ℓ. All energy eigenvalues are negative because they correspond to bound states. All states associated with a given principal quantum number n form an atomic shell n. All states in a given atomic shell have one or more atomic subshells ℓ. These subshells are depicted in this figure in form of a horizontal line. The nomenclature of atomic shells and subshells from spectroscopy is widely used also for other atoms in physics and chemistry .

Any atom in an excited energy state can transition to a lower energy state by emitting a photon. These photons are detected in spectroscopy and interpreted. The spectroscopic notation was introduced before quantum mechanics has been developed. The $\ell = 0$ states are denoted by the letter s coming from the word “sharp” to describe the observed spectral lines, the $\ell = 1$ states are denoted by the letter p coming from the word “principal”, the $\ell = 2$ states are denoted by the letter d from “diffuse”, the $\ell = 3$ states are denoted by the letter f from “fundamental”, and all the following ℓ states are denoted alphabetically starting from g. Thus, the horizontal lines in figure 2 are labeled accordingly. The $\ell = 0$ state is 1s for $n = 1$, is 2s for $n = 2$ and so on, the $\ell = 1$ state is 2p for $n = 2$ and 3p for $n = 3$ because there is no $\ell = 1$ state for $n = 1$, and so on.