Lecture notes: QM 07

Hydrogen Atom

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Contents

A hydrogen atom or a hydrogen like atom (He^+, Li^{2+}, Be^{+3}, etc.) consists of an atomic nucleus of charge Ze and an electron of charge $-e$. Their mutual interaction is given by the Coulomb potential

$$V(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{1}$$

where $\mathbf{r}_1 = \mathbf{r}_1(x_1, y_1, z_1)$ and $\mathbf{r}_2 = \mathbf{r}_2(x_2, y_2, z_2)$ are the electron and nucleus position vectors, respectively. The time-independent Schrödinger equation for the system is given by

$$\left\{-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|)\right\}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E_{\text{tot}}\Psi(\mathbf{r}_1, \mathbf{r}_2), \tag{2}$$

where m_1 and m_2 are the masses of electron and nucleus, respectively and the Laplacians are given in cartesian coordinate as

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}; \qquad i = 1, 2. \tag{3}$$

1 Separation of the Center of Mass Motion

Since V depends only on the relative distance between the electron and nucleus, instead of the position vectors of the electron and nucleus, it is more appropriate to use the coordinates of the center of mass, $\mathbf{R} = \mathbf{R}(X, Y, Z)$, and the relative coordinates of the electron with respect to the nucleus, $\mathbf{r} = \mathbf{r}(x, y, z)$. The transformation from coordinates ($\mathbf{r}_1$, $\mathbf{r}_2$) to coordinates ($\mathbf{R}$, $\mathbf{r}$) is given by introducing the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{4}$$

and the vector

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{5}$$

which determines the position of the centre of mass system. We write $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$ to show

$$\frac{\partial\Psi}{\partial x_1} = \frac{\partial X}{\partial x_1}\cdot\frac{\partial\Psi}{\partial X} + \frac{\partial x}{\partial x_1}\cdot\frac{\partial\Psi}{\partial x} = \frac{\mu}{m_2}\frac{\partial\Psi}{\partial X} + \frac{\partial\Psi}{\partial x}. \tag{6}$$

In three dimension

$$\nabla_1 = \frac{\mu}{m_2}\nabla_R + \nabla \tag{7}$$

where μ is the reduced mass defined as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}. \tag{8}$$

Similarly ∇_2 can be written as

$$\nabla_2 = \frac{\mu}{m_1}\nabla_R - \nabla. \tag{9}$$

Changing variables from the coordinates $(\mathbf{r}_1, \mathbf{r}_2)$ to the new coordinates $(\mathbf{R}, \mathbf{r})$, we find

$$\begin{aligned}\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2 &= \frac{\hbar^2}{2m_1}\left(\frac{\mu}{m_2}\nabla_R + \nabla\right)^2 + \frac{\hbar^2}{2m_2}\left(\frac{\mu}{m_1}\nabla_R - \nabla\right)^2 \\ &= \frac{\hbar^2}{2M}\nabla_R^2 + \frac{\hbar^2}{2\mu}\nabla^2\end{aligned} \tag{10}$$

where $M = m_1 + m_2$ is the total mass of the system. The Schrödinger equation (2) therefore becomes

$$\left\{-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right\}\Psi(\mathbf{R}, \mathbf{r}) = E_{\text{tot}}\Psi(\mathbf{R}, \mathbf{r}). \tag{11}$$

At this moment we pause for a while and examine our variables in a bit details. We started with $\mathbf{r}_1$ and $\mathbf{r}_2$, the electron and nucleus positions vectors respectively. If we denote the momenta vectors of electro and nucleus by $\mathbf{p}_1$ and $\mathbf{p}_2$ respectively, then we

have two pairs of canonical variables, meaning they satisfy the canonical commutation relations:

$$\begin{aligned}[(\hat{\mathbf{r}}_1)_i,\, (\hat{\mathbf{p}}_1)_j] &= i\hbar\delta_{ij},\\ [(\hat{\mathbf{r}}_2)_i,\, (\hat{\mathbf{p}}_2)_j] &= i\hbar\delta_{ij}.\end{aligned} \tag{12}$$

Here the subscripts $i, j = 1, 2, 3$ denote the various components of the vector operators. Furthermore, the proton variables commute with the electron variables. We have two pairs of independent canonical variables.

After center of mass (CM) motion separation we arrived at the Schrödinger equation (11) where the new position vectors are $\mathbf{r}$ and $\mathbf{R}$, the relative and CM position vectors respectively. To find the corresponding momenta vectors we make use of the equations (7) and (9) along with the definition of momentum operator in three dimension

$$\hat{\mathbf{p}} = -i\hbar\nabla \tag{13}$$

to have

$$\hat{\mathbf{p}}_1 = \frac{\mu}{m2}\hat{\mathbf{P}} + \hat{\mathbf{p}}, \tag{14}$$

and

$$\hat{\mathbf{p}}_2 = \frac{\mu}{m1}\hat{\mathbf{P}} - \hat{\mathbf{p}}. \tag{15}$$

Solving equations (14) and (15) and dropping the operator symbol we have the momenta vectors which correspond to the coordinates (4) and (5) respectively,

$$\begin{aligned}\mathbf{p} &= \mu\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right) = \frac{m_2}{M}\mathbf{p}_1 - \frac{m_1}{M}\mathbf{p}_2,\\ \mathbf{P} &= \mathbf{p}_1 + \mathbf{p}_2.\end{aligned} \tag{16}$$

These new sets of variables are also canonical that is they satisfy the following commutation relations.

$$\begin{aligned}[\hat{\mathbf{r}}_i,\, \hat{\mathbf{p}}_j] &= i\hbar\delta_{ij},\\ \left[\hat{\mathbf{R}}_i,\, \hat{\mathbf{P}}_j\right] &= i\hbar\delta_{ij}.\end{aligned} \tag{17}$$

The relative coordinates variables also commute with the CM coordinates. Therefore, we again have two pairs of independent canonical variables.

Since $\mathbf{R}$ and $\mathbf{r}$ are independent to each other the wave function $\Psi(\mathbf{R}, \mathbf{r})$ can be separated into a product of functions of the centre of mass coordinate $\mathbf{R}$ and of relative coordinate $\mathbf{r}$ as $\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\psi(\mathbf{r})$. With this the Schrödinger equation (11) can be written as

$$\left\{-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right\}\Phi(\mathbf{R})\psi(\mathbf{r}) = E_{\text{tot}}\Phi(\mathbf{R})\psi(\mathbf{r})$$

or

$$-\frac{\hbar^2}{2M}\psi(\mathbf{r})\nabla_R^2\,\Phi(\mathbf{R}) + \Phi(\mathbf{R})\left\{-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right\}\psi(\mathbf{r}) = E_{\text{tot}}\Phi(\mathbf{R})\psi(\mathbf{r})$$

or

$$-\frac{\hbar^2}{2M}\frac{1}{\Phi(\mathbf{R})}\nabla_R^2\,\Phi(\mathbf{R})+\frac{1}{\psi(\mathbf{r})}\left\{-\frac{\hbar^2}{2\mu}\nabla^2+V(r)\right\}\psi(\mathbf{r})=E_{\text{tot}}. \tag{18}$$

Thus, we have the following two separate equations

$$-\frac{\hbar^2}{2M}\nabla_R^2\,\Phi(\mathbf{R})=E_{\text{CM}}\Phi(\mathbf{R}) \tag{19}$$

and

$$\left\{-\frac{\hbar^2}{2\mu}\nabla^2+V(r)\right\}\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{20}$$

with the condition $E_{\text{tot}}=E_{\text{CM}}+E$.

Thus, we have reduced the Schrödinger equation (11), which involves two variables $\mathbf{R}$ and $\mathbf{r}$, into two separate equations (19) and (20) each involving a single variable. Note that equation (19) shows that the center of mass moves like a free particle of mass M. The solution to this kind of equation has the form

$$\Phi(\mathbf{R})=(2\pi)^{-3/2}\,e^{i\mathbf{k}\cdot\mathbf{R}} \tag{21}$$

where $\mathbf{k}$ is the wave vector associated with the center of mass. The constant $E_{\text{CM}}=\hbar^2k^2/(2M)$ gives the kinetic energy of the center of mass in the laboratory system (the total mass M is located at the origin of the center of mass coordinate system).

The second equation (20) represents the Schrödinger equation of a fictitious particle of mass μ moving in the central potential

$$V(r)=-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}. \tag{22}$$

We should note that the total wave function $\Psi(\mathbf{R},\mathbf{r})$ is seldom used. When the hydrogen like problem is mentioned, this implicitly refers to $\psi(r)$ and E. That is, the hydrogenic wave function and energy are taken to be given by $\psi(r)$ and E, not by $\Psi(\mathbf{R},\mathbf{r})$ and E_{tot} This is because nucleus is much massive then electron and compare to the motion of electron nucleus remain stationary. Since we are only interested to the motion of electron the Schrödinger equation of the hydrogen like atom is given by (20).

2 Separation of the Schrödinger Equation in Spherical Polar Coordinates

The Schrödinger equation (20) for the relative motion has the form of an equation for a central potential with Hamiltonian

$$\begin{aligned}H &= -\frac{\hbar^2}{2\mu}\nabla^2+V(r)\\ &= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+V(r)\\ &= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\mathbf{L}^2}{\hbar^2r^2}\right]+V(r),\end{aligned} \tag{23}$$

where $\mathbf{L}^2$ is the square of the magnitude of the orbital angular momentum and defined as

$$\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{24}$$

The corresponding time-independent Schrödinger equation is

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{\hbar^2 r^2} \right] + V(r) \right\} \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

or

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\mathbf{L}^2}{2\mu r^2} + V(r) \right\} \psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{25}$$

In order to simplify the solution of this equation we notice that $\mathbf{L}^2$ do not operate on the radial variable r. Since the spherical harmonics $Y_{lm}(\theta, \phi)$ are eigenfunctions of $\mathbf{L}^2$ we can look for solution of the Schrödinger equation (25) having the separable form

$$\psi(\mathbf{r}) = \psi(r, \theta, \psi) = R_l(r) Y_{lm}(\theta, \phi) \tag{26}$$

where $R_l(r)$ is the radial function which remains to be found. It is worth stressing that the angular dependence of the eigenfunction (26) is entirely given by the spherical harmonics $Y_{lm}(\theta, \phi)$ characterised by the orbital angular momentum quantum number l and magnetic quantum number m.

3 Solution of the Radial Equation

Inserting (26) into the Schrödinger equation (25) and using the fact that $\mathbf{L}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi)$, we obtain for the radial function the differential equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) \right\} R_l(r) = E R_l(r). \tag{27}$$

Note that the magnetic quantum number m does not appear in this equation. Therefore the radial function is independent of this quantum number. In the domain of the variable r, the angular momentum contribution $\hbar^2 l(l+1)/(2\mu r^2)$ acts as an effective addition to the potential energy. It can be identified with centrifugal force, which pulls the electron outward, in opposition to the Coulomb attraction. Carrying out the successive differentiations in (27) and simplifying, we obtain

$$\left\{ -\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right\} R_l(r) = E R_l(r)$$

or

$$-\frac{\hbar^2}{2\mu} \left(\frac{d^2 R_l(r)}{dr^2} + \frac{2}{r} \frac{dR_l(r)}{dr} \right) + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} - E \right] R_l(r) = 0$$

or

$$\frac{d^2 R_l(r)}{dr^2} + \frac{2}{r} \frac{dR_l(r)}{dr} + \left[\frac{2\mu}{\hbar^2} E - \frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{1}{r} \right] R_l(r) = 0 \tag{28}$$

another second-order linear differential equation with non-constant coefficients.

3.1 Asymptotic solution of the radial wave function

First we explore the asymptotic solutions to (28), as $r \to \infty$. In the asymptotic approximation,

$$\frac{d^2R_l(r)}{dr^2} \approx -\frac{2\mu E}{\hbar^2}R_l(r) = \frac{2\mu|E|}{\hbar^2}R_l(r) \tag{29}$$

having noted that the energy E is negative for bound states. Solutions to (29) are

$$R_l(r) = Ae^{-\sqrt{2\mu|E|/\hbar^2}\,r} + Be^{\sqrt{2\mu|E|/\hbar^2}\,r}, \tag{30}$$

where A and B are constants to be determined. We reject the positive exponential on physical grounds, since $R_l(r) \to \infty$ as $r \to \infty$, in violation of the requirement that the wave function must be finite everywhere. Choosing the negative exponential ($B = 0$) and setting

$$E = -\frac{\mu Z^2 e^4}{8\epsilon_0^2 h^2} = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2\hbar^2}, \tag{31}$$

the ground state energy in the Bohr theory (in center of mass system), we obtain

$$R_l(r) = Ae^{-Zr/a_\mu} \tag{32}$$

where a_μ is the modified Bohr radius

$$a_\mu = \frac{(4\pi\epsilon_0)\hbar^2}{\mu e^2} = \frac{\epsilon h^2}{\pi\mu e^2} = \frac{m_1}{\mu}\frac{\epsilon h^2}{\pi m_1 e^2} = \frac{m_1}{\mu}a_0 \tag{33}$$

with a_0 being the Bohr radius.

It turns out, very fortunately, that this asymptotic approximation is also an exact solution of the Schrödinger equation (28) with $l = 0$. The solutions to (28), designated $R_{nl}(r)$, are labelled by n, known as the principal quantum number, as well as by the orbital angular momentum l, which is a parameter in the radial equation. The solution (32) corresponds to $R_{10}(r)$. This should be normalized according to the condition

$$\int_0^\infty [R_{10}(r)]^2 r^2 dr = 1. \tag{34}$$

Using the definite integral $\int_0^\infty r^n e^{-\alpha r}dr = n!\alpha^{-(n+1)}$, we get the normalized radial function

$$R_{10}(r) = 2\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu}. \tag{35}$$

Since this function is nodeless, we identify it with the ground state of the hydrogen like atom. Multiplying (35) by the spherical harmonic $Y_{00}(\theta,\phi) = 1/\sqrt{4\pi}$, we obtain the total wave function

$$\psi_{100}(r,\theta,\phi) = \psi_{100}(r) = \psi_{1s}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu}. \tag{36}$$

The wave function of the hydrogen atom in ground state is found from (36) by setting $Z = 1$ as

$$\psi_{1s}(r) = \left(\frac{1}{\pi^{1/3}a_\mu}\right)^{3/2} e^{-r/a_\mu}. \tag{37}$$

3.2 General solution of the radial wave function

The normalized radial function for the bound state of hydrogenic atom has a rather complicated form which we give without proof:

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2} e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{38}$$

with

$$\rho = \frac{2Z}{na_\mu}r, \qquad a_\mu = \frac{(4\pi\epsilon_0)\hbar^2}{\mu e^2}.$$

Here L_β^α is an associated Laguerre polynomial. The first few radial eigenfunctions (38) are given by

$$R_{10}(r) = 2\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu} \tag{39}$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_\mu}\right)^{3/2}\left(1-\frac{Zr}{2a_\mu}\right) e^{-Zr/2a_\mu} \tag{40}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right) e^{-Zr/2a_\mu} \tag{41}$$

$$R_{30}(r) = 2\left(\frac{Z}{3a_\mu}\right)^{3/2}\left(1-\frac{2Zr}{3a_\mu}+\frac{2Z^2r^2}{27a_\mu^2}\right) e^{-Zr/3a_\mu} \tag{42}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9}\left(\frac{Z}{3a_\mu}\right)^{3/2}\left(1-\frac{Zr}{6a_\mu}\right)\left(\frac{Zr}{a_\mu}\right) e^{-Zr/3a_\mu} \tag{43}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right)^2 e^{-Zr/3a_\mu} \tag{44}$$

and are illustrated in Fig. 1.

4 The Hydrogenic Wave Function

The solutions of the hydrogenic Schrödinger equation in spherical polar coordinates can now be written in full

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{45}$$

where $n = 1, 2, 3, \ldots$ is the principle quantum number, $l = 0, 1, 2, \ldots, n-1$ is the orbital angular momentum quantum number and $m = 0, \pm1, \pm2 \ldots \pm l$ is the magnetic quantum number.

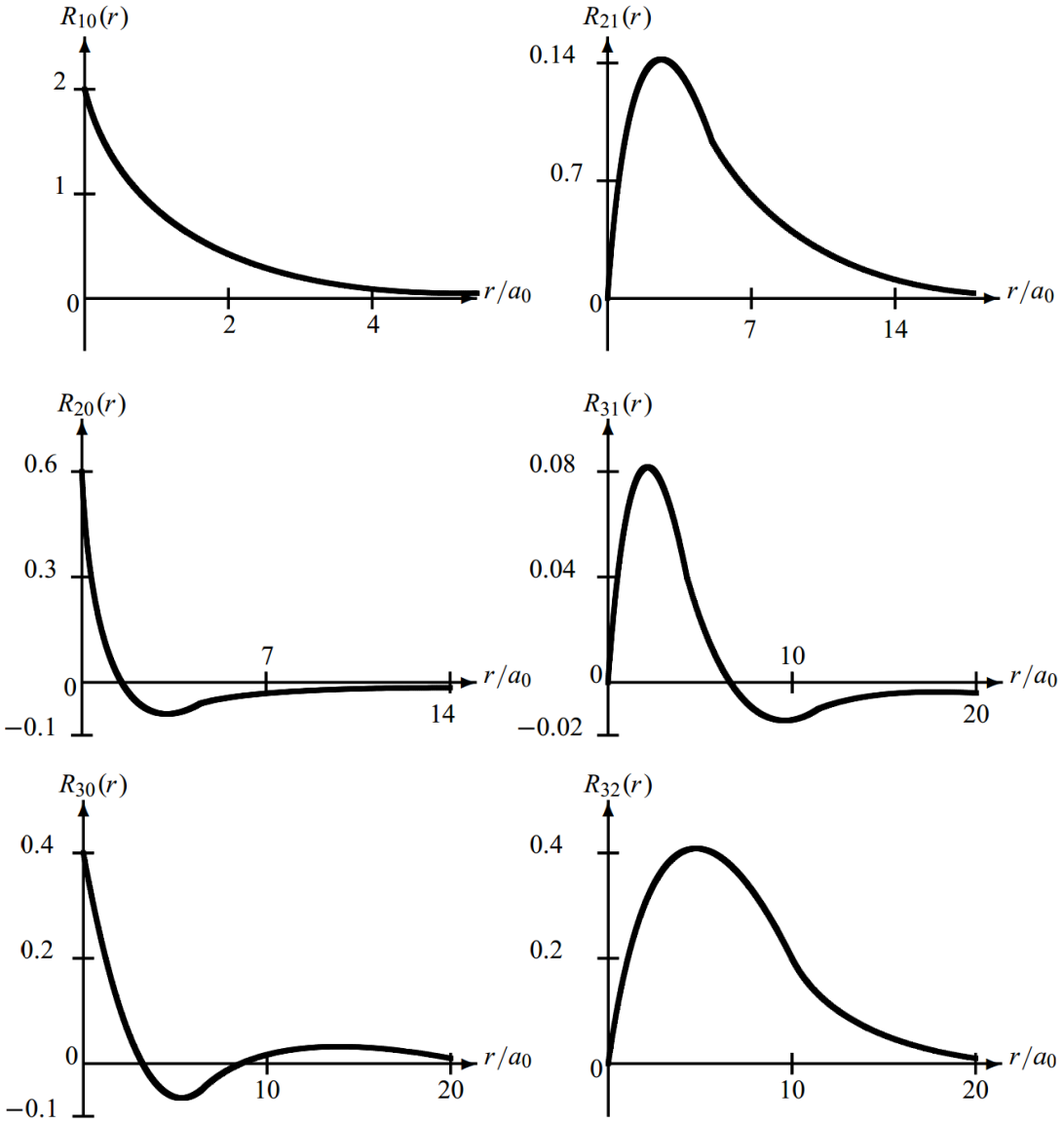

Figure 1: The first few radial functions $R_{nl}(r)$ for hydrogen. The radial length is in units of the Bohr radius a_0. Notice that $R_{nl}(r)$ has $(n - l - 1)$ nodes. [2]

References

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