Quantum Mechanics I

PHY 3103

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The Hydrogen Like Atom

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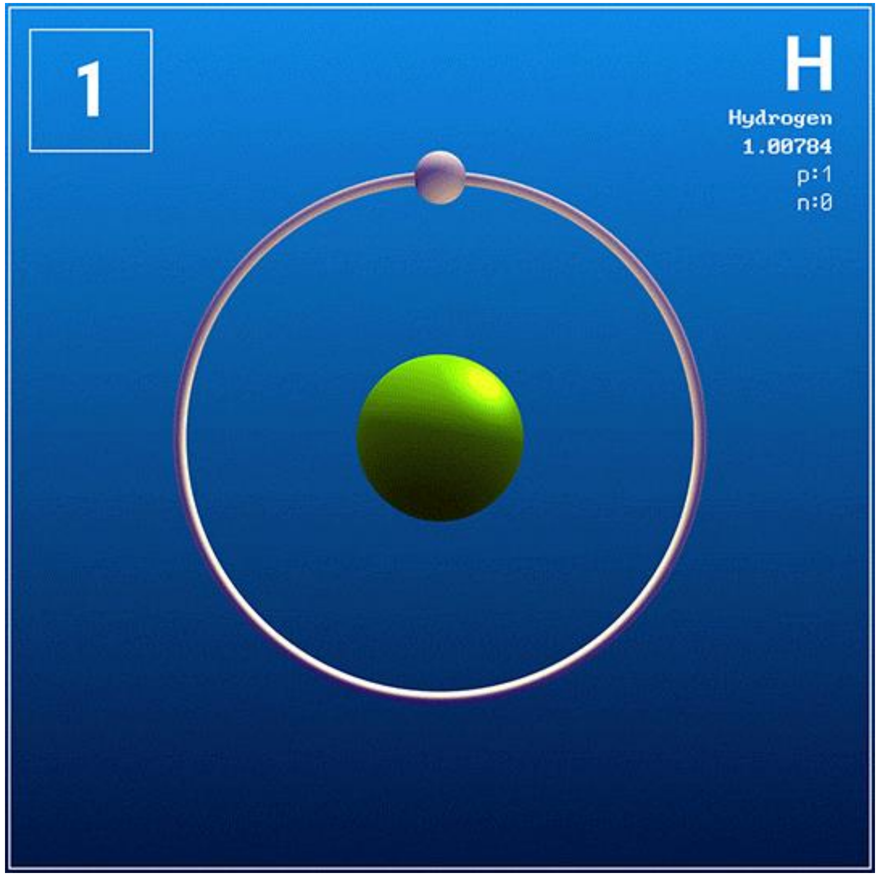
Hydrogen atom



Wikipedia

Particle	Position	Momentum
Electron	$\mathbf{r}_1$	$\mathbf{p}_1$
Proton	$\mathbf{r}_2$	$\mathbf{p}_2$

$$[(\hat{\mathbf{r}}_1)_i,\ (\hat{\mathbf{p}}_1)_j] = i\hbar\delta_{ij}$$

$$[(\hat{\mathbf{r}}_2)_i,\ (\hat{\mathbf{p}}_2)_j] = i\hbar\delta_{ij}$$

The Hydrogenic Atom

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

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

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 Schrödinger equation

The time-independent Schrödinger equation for the system is given by

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

where m_1 and m_2 are the masses of electron and nucleus.

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

Wave function

Particle	Position	Momentum
Electron	$\mathbf{r}_1$	$\mathbf{p}_1$
Proton	$\mathbf{r}_2$	$\mathbf{p}_2$

Wave function: $\Psi(\mathbf{r}_1,\, \mathbf{r}_2)$

Normalization: $\int \Psi^*(\mathbf{r}_1,\, \mathbf{r}_2)\Psi(\mathbf{r}_1,\, \mathbf{r}_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 = 1$

Separation of the Center of Mass Motion

The transformation from coordinates ($\mathbf{r}_1$, $\mathbf{r}_2$) to coordinates ($\mathbf{R}$, $\mathbf{r}$) is given by introducing the relative coordinate

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

and the vector

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

which determines the position of the centre of mass system.

Change of variables

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

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

where μ is the reduced mass defined as

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

Change of variables in 3D

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

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

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

The kinetic energy operators

$$\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2 = \frac{\hbar^2}{2M}\nabla_R^2 + \frac{\hbar^2}{2\mu}\nabla^2$$

where $M = m_1 + m_2$ is the total mass of the system.

The Schrödinger equation in new 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 can be written as

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

Momentum operators corresponding to **r** and **R**

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

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

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

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

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

Momentum operators corresponding to **r** and **R**

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

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

$$\mathbf{p} = \mu\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right) = \frac{m_2}{M}\mathbf{p}_1 - \frac{m_1}{M}\mathbf{p}_2,$$

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2.$$

Momentum operators corresponding to **r** and **R**

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

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

Canonical variables

$$[(\hat{\mathbf{r}}_1)_i,\ (\hat{\mathbf{p}}_1)_j] = i\hbar\delta_{ij}$$

$$[(\hat{\mathbf{r}}_2)_i,\ (\hat{\mathbf{p}}_2)_j] = i\hbar\delta_{ij}$$

$$[\hat{\mathbf{r}}_i,\ \hat{\mathbf{p}}_j] = i\hbar\delta_{ij},$$

$$\left[\hat{\mathbf{R}}_i,\ \hat{\mathbf{P}}_j\right] = i\hbar\delta_{ij}.$$

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

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

$$\mathbf{p} = \mu\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right)$$

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2.$$

Canonical variables

Change of variables in 3D

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

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

$$\boxed{\nabla_2 = \frac{\mu}{m_1}\nabla_R - \nabla}$$

The kinetic energy operators

$$\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2 = \frac{\hbar^2}{2M}\nabla_R^2 + \frac{\hbar^2}{2\mu}\nabla^2$$

where $M = m_1 + m_2$ is the total mass of the system.

The Schrödinger equation in new variables

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

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

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

Two separate Schrödinger equations

Thus, we have the following two separate equations

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

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

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

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

The center of mass equation

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

The solution to this kind of equation has the form

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

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 Hamiltonian in spherical polar coordinates

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

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

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

The time-independent Schrödinger equation

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

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 having the separable form

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

where $R_l(r)$ is the radial function which remains to be found.

Spherical harmonics $Y_{lm}(\theta, \phi)$

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi)$$

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\left(\frac{2l+1}{4\pi}\right) \frac{(l-m)!}{(l+m)!}}\, P_l^m(\cos\theta)\, e^{im\phi}, \qquad (m \geq 0).$$

Here $P_l^m(\cos\theta)$ is the associated Legendre functions. $m < 0$, we use

$$Y_{l,m}(\theta, \phi) = (-1)^m [Y_{l,-m}(\theta, \phi)]^*.$$

$$\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \, \sin\theta \, Y^*_{l'm'}(\theta, \phi)\, Y_{lm}(\theta, \phi) = (Y^*_{l'm'},\, Y_{lm}) = \delta_{l'l}\, \delta_{m'm}.$$

Solution of the Radial Equation

$$\mathbf{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1) Y_{lm}(\theta,\phi)$$

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

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

Asymptotic solution of the Radial Equation

Asymptotic solution: $r \to \infty$

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

having noted that the energy E is negative for bound states.

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

where A and B are constants to be determined.

Asymptotic solution of the Radial Equation

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

Choose the negative exponential ($B = 0$) and set

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

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

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

Asymptotic solution of the Radial Equation

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

where a_μ is the modified Bohr radius

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

with a_0 being the Bohr radius.

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

$$\int_0^\infty r^n e^{-\alpha r} dr = n! \alpha^{-(n+1)}$$

Normalized radial function

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

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

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) \; = \; \hbar^2 l(l+1) Y_{lm}(\theta, \phi)$$

The wave function ψ_{1s}

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

$$Y_{00}(\theta, \phi) = 1/\sqrt{4\pi}$$

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

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

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

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:

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

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.

Radial eigenfunctions of hydrogenic atom

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

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

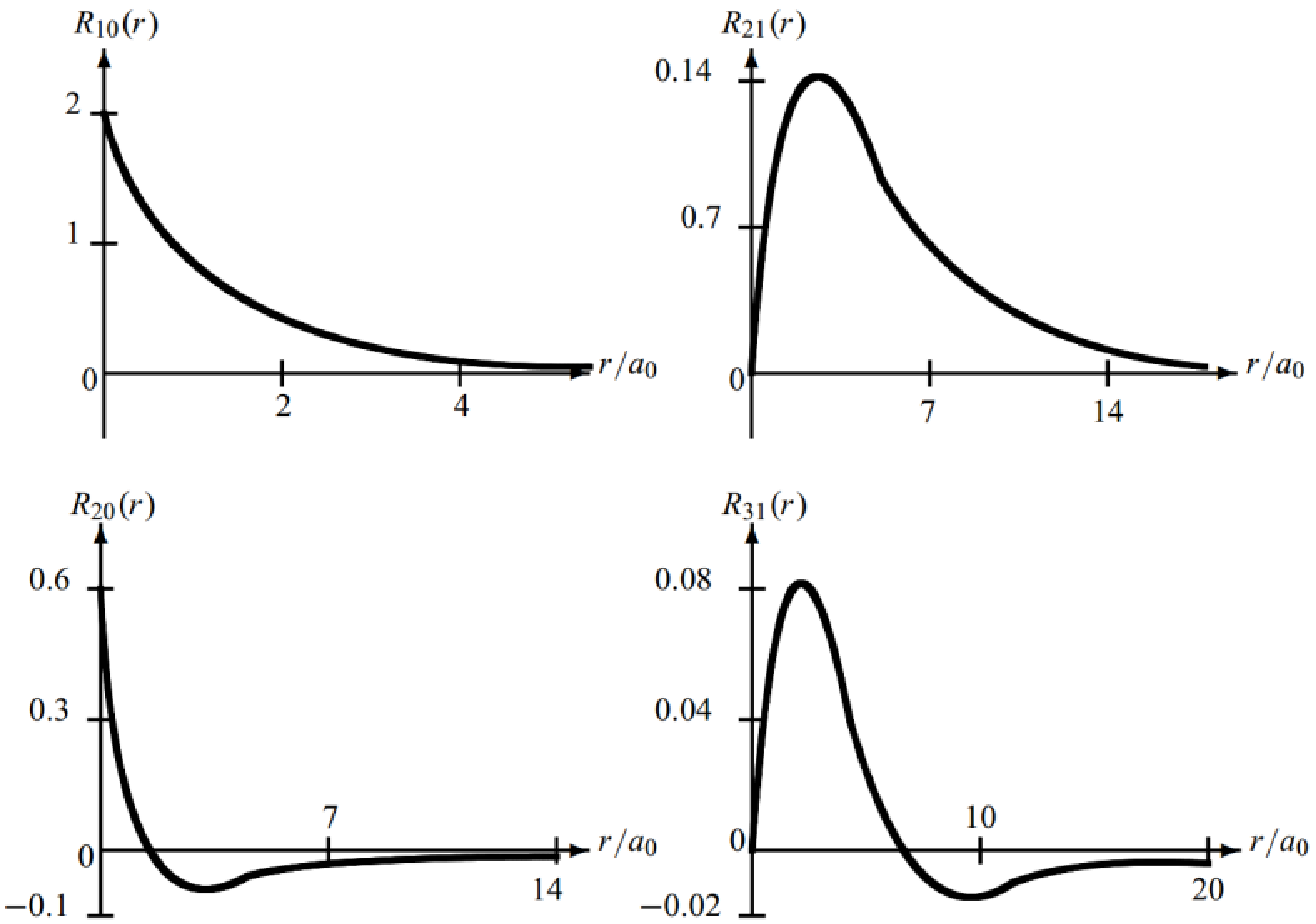
$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_\mu}\right)^{3/2}\left(\frac{Zr}{a_\mu}\right) e^{-Zr/2a_\mu}$$

Radial eigenfunctions of hydrogenic atom

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

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

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



R10(r)
2
1
0
2
4
r/a0
R21(r)
0.14
0.7
0
7
14
r/a0
R20(r)
0.6
0.3
0
−0.1
7
14
r/a0
R31(r)
0.08
0.04
0
−0.02
10
20
r/a0

The hydrogenic wave function

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

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

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 $m = 0, \pm 1, \pm 2 \ldots \pm l$ is the magnetic quantum number.