Chapter 7
Central Forces in Quantum Mechanics

Radially symmetric problems appear if the interaction between two particles depends only on their separation r. We will first see how the dynamical problem of the motion of the two particles can be separated in terms of center of mass motion and relative motion and then write the effective Hamiltonian for the relative motion of the two particles in spherical coordinates.

7.1 Separation of center of mass motion and relative motion

The separation of center of mass motion and relative motion proceeds like in classical mechanics. The Hamiltonian of the 2-particle system is

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(|\mathbf{x}_1 - \mathbf{x}_2|) = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(r), \tag{7.1}$$

where

$$M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7.2}$$

are the total and reduced mass,

$$\mathbf{R} = \frac{m_1\mathbf{x}_1 + m_2\mathbf{x}_2}{m_1 + m_2}, \quad \mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2 \tag{7.3}$$

are the operators for center of mass and relative coordinates, and

$$\mathbf{P} = M\dot{\mathbf{R}} = \mathbf{p}_1 + \mathbf{p}_2, \quad \mathbf{p} = \mu\dot{\mathbf{r}} = \frac{\mu}{m_1}\mathbf{p}_1 - \frac{\mu}{m_2}\mathbf{p}_2 = \frac{m_2\mathbf{p}_1 - m_1\mathbf{p}_2}{m_1 + m_2} \tag{7.4}$$

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are the momentum operators of center of mass motion and relative motion. The relative motion of the two original particles also comes with an angular momentum

$$\boldsymbol{l} = \mathbf{x}_1 \times \mathbf{p}_1 + \mathbf{x}_2 \times \mathbf{p}_2 - \mathbf{R} \times \mathbf{P} = \mathbf{r} \times \mathbf{p}. \tag{7.5}$$

The inverse transformations are

$$\mathbf{x}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r}, \quad \mathbf{x}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}, \quad \mathbf{p}_1 = \frac{m_1}{M}\mathbf{P} + \mathbf{p}, \quad \mathbf{p}_2 = \frac{m_2}{M}\mathbf{P} - \mathbf{p}, \tag{7.6}$$

and if we assume $m_2 \geq m_1$,

$$m_2 = \frac{M + \sqrt{M(M-4\mu)}}{2}, \quad m_1 = \frac{M - \sqrt{M(M-4\mu)}}{2}.$$

The ∇ operators transform as

$$\frac{\partial}{\partial \boldsymbol{R}} = \frac{\partial}{\partial \boldsymbol{x}_1} + \frac{\partial}{\partial \boldsymbol{x}_2}, \quad \frac{\partial}{\partial \boldsymbol{r}} = \frac{m_2}{M}\frac{\partial}{\partial \boldsymbol{x}_1} - \frac{m_1}{M}\frac{\partial}{\partial \boldsymbol{x}_2},$$
$$\frac{\partial}{\partial \boldsymbol{x}_1} = \frac{m_1}{M}\frac{\partial}{\partial \boldsymbol{R}} + \frac{\partial}{\partial \boldsymbol{r}}, \quad \frac{\partial}{\partial \boldsymbol{x}_1} = \frac{m_2}{M}\frac{\partial}{\partial \boldsymbol{R}} - \frac{\partial}{\partial \boldsymbol{r}}.$$

These are the same transformations for operators as the corresponding transformations for classical coordinates and momenta in classical mechanics. From the quantum mechanics perspective this is not surprising, since the transformation equations for the operators are linear and therefore also hold for the expectation values of the operators, hence for the classical variables. What becomes particularly relevant for quantum mechanics is that the transformations preserve canonical commutation relations,

$$[\mathbf{x}_1, \mathbf{p}_1] = \mathrm{i}\hbar\underline{1}, \; [\mathbf{x}_2, \mathbf{p}_2] = \mathrm{i}\hbar\underline{1} \quad \Leftrightarrow \quad [\mathbf{R}, \mathbf{P}] = \mathrm{i}\hbar\underline{1}, \; [\mathbf{r}, \mathbf{p}] = \mathrm{i}\hbar\underline{1}.$$

Since the interaction does not depend on the center of mass coordinates, we can separate the center of mass motion with momentum $\boldsymbol{P} = \hbar\boldsymbol{K}$ in the wave function for the time-independent Schrödinger equation,

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2\pi}^3}\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})\psi(\boldsymbol{r}), \tag{7.7}$$

and the energy eigenvalue problem $H|\Psi\rangle = E_{\text{total}}|\Psi\rangle$ reduces to an eigenvalue problem for the relative motion,

$$E\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2\mu}\Delta\psi(\boldsymbol{r}) + V(r)\psi(\boldsymbol{r}), \tag{7.8}$$

where

$$E_{\text{total}} = E + \frac{\hbar^2\boldsymbol{K}^2}{2M} \tag{7.9}$$

is the total energy in the center of mass motion and relative motion.

The discussion of separated solutions in Section 5.5 implies that the solutions for the Hamiltonian (7.1) should have the separated form with respect to center of mass motion and relative motion, $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2) = \Psi(\boldsymbol{R})\psi(\boldsymbol{r})$. However, the reasoning there also implies that we cannot find a solution of the Schrödinger equation which is separated in the actual coordinates of the two particles, $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2) \neq \psi_2(\boldsymbol{x}_2)\psi_1(\boldsymbol{x}_1)$. The wave functions of interacting particles are always entangled. This entanglement is easy to understand. Suppose that the interaction between two particles is attractive and strong enough to generate a bound state between the two particles. If we observe one particle at location $\boldsymbol{x}_1$, we know that the second particle has to be nearby at a location which is determined probabilistically by $|\psi(\boldsymbol{x}_1 - \boldsymbol{x}_2)|^2$. On the other hand, if the interaction is weak or repulsive, interactions with other particles will soon dominate each of the two particles, and their two-particle wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2) = \Psi(\boldsymbol{R})\psi(\boldsymbol{r})$ is not a viable description any more: their mutual entanglement is destroyed by interactions with other particles.

We have based this discussion on the wave function (7.7) which appears in the $(\boldsymbol{x}_1,\boldsymbol{x}_2)$ representation of the time-independent two-particle Schrödinger equation $H|\Psi\rangle = E_{\mathrm{total}}|\Psi\rangle$ with the Hamiltonian (7.1). If one starts from a time-dependent two-particle Schrödinger equation

$$\begin{aligned} \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) = &-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial \boldsymbol{x}_1^2}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial \boldsymbol{x}_2^2}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) \\ &+ V(|\boldsymbol{x}_1 - \boldsymbol{x}_2|)\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t), \end{aligned}$$

the separation *ansatz* for the center of mass motion

$$\begin{aligned} \Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) &= \Psi(\boldsymbol{x}_1,\boldsymbol{x}_2)\exp\!\left(-\mathrm{i}\frac{E_{\mathrm{total}}}{\hbar}t\right) \\ &= \frac{1}{\sqrt{2\pi}^3}\exp\!\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} - \mathrm{i}\frac{\hbar\boldsymbol{K}^2}{2M}t\right)\psi(\boldsymbol{r},t) \\ &= \frac{1}{\sqrt{2\pi}^3}\exp\!\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} - \mathrm{i}\frac{\hbar\boldsymbol{K}^2}{2M}t\right)\psi(\boldsymbol{r})\exp\!\left(-\mathrm{i}\frac{E}{\hbar}t\right) \end{aligned}$$

leads again to equation (7.8).

Separation of the center of mass motion in the present form works for any potential $V(\boldsymbol{r})$ which only depends on the separation vector $\boldsymbol{r}$ of the two particles. More general, if the 2-particle system moves in a potential of the form

$$V(\boldsymbol{x}_1,\boldsymbol{x}_2) = V(\boldsymbol{r}) + W(\boldsymbol{R}),$$

we can separate center of mass motion in the potential $W(\boldsymbol{R})$ from relative motion with the interaction potential $V(\boldsymbol{r})$ and find two independent effective single-particle Schrödinger equations (or Newton equations in mechanics) for the system. An example for this situation would be a hydrogen atom trapped in a potential well, e.g. in ice. If we model the potential well through a three-dimensional oscillator potential, the center of mass motion could be described by oscillator eigenstates

$\Psi_N(\boldsymbol{R},t)$ while the relative motion between the electron and the proton would be described by the wave functions $\psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)\exp(-\mathrm{i}E_nt/\hbar)$ derived in Sections 7.5 and 7.8.

7.2 The concept of symmetry groups

The effective single particle equation (7.8) for relative motion has the same form in every coordinate system which is related to the coordinates $\boldsymbol{r}$ through a rotation $r'^i = R^i{}_a r^a$, or in column vector notation,

$$\boldsymbol{r}' = \underline{R}\cdot\boldsymbol{r}, \quad \underline{R}^T\cdot\underline{R} = \underline{1},$$

cf. Section 4.1 and in particular equations (4.6) and (4.8). Contrary to Section 4.1, here we use the common left multiplication convention for linear coordinate transformations, $r^a \to r'^i = R^i{}_a r^a$, i.e. our rotation matrix $\underline{R}$ in the present section corresponds to $\underline{R}^T = \underline{R}^{-1}$ in Section 4.1.

Rotations have the following four basic properties:

1. The combination of two rotations $\underline{R}_1$ and $\underline{R}_2$ yields again a rotation $\underline{R}_2\cdot\underline{R}_1$,

$$\boldsymbol{r}'' = \underline{R}_2\cdot\boldsymbol{r}' = \underline{R}_2\cdot(\underline{R}_1\cdot\boldsymbol{r}) = (\underline{R}_2\cdot\underline{R}_1)\cdot\boldsymbol{r}.$$

2. The identity transformation $\underline{1}$ is a particular rotation.
3. For every rotation there is an inverse rotation, $\underline{R}^{-1}\cdot\underline{R} = \underline{1}$.
4. Combination of rotations is associative,

$$\underline{R}_3\cdot(\underline{R}_2\cdot\underline{R}_1) = (\underline{R}_3\cdot\underline{R}_2)\cdot\underline{R}_1.$$

These four algebraic properties are common to all sets of symmetry transformations of physical systems, and they have far reaching consequences in the sense that many other interesting properties of symmetry transformations can be derived from these four properties. Every set of mathematical objects having these four properties is therefore denoted as a *group*, and the study of groups is a subdiscipline of algebra denoted as group theory.

Groups which are particularly relevant for quantum mechanics include the following sets:

1. The group of proper rotations is the set of all rotations which does not include inversion of an odd number of axes. Matrices which generate proper rotations do not only satisfy the orthogonality condition

$$\underline{R}^T\cdot\underline{R} = \underline{1},$$

but also the special additional condition

$$\det\underline{R} = 1.$$

The group of proper rotations in three dimensions is therefore also denoted as the *special orthogonal group of rotations in three dimensions*, or SO(3) for short.

2. A group which is closely related to the group SO(3) is the group of unitary 2 × 2 matrices with determinant 1,

$$\underline{U}^{+}\cdot\underline{U}=\underline{1},\quad \det\underline{U}=1.$$

   This is the *special group of unitary transformations in two dimensions* SU(2).
3. The Poincaré group and its various subgroups, including in particular the proper orthochronous Lorentz group SO(1,3) of proper rotations and Lorentz boosts in Minkowski spacetime, are important for relativistic quantum mechanics.
4. SO(1,3) is closely related to the group of complex 2 × 2 matrices with determinant 1. This group is often denoted as SL(2,ℂ).
5. Discrete symmetry groups involve e.g. translations along lattice vectors in a regular lattice, or inversions of axes, or rotations by fixed angles. Discrete groups are also important in many applications of quantum mechanics.
6. The known basic particle interactions (besides gravity) are related to the group U(1) of phase transformations, and also to the special unitary groups SU(2) and SU(3).

In this and the following chapter we are primarily concerned with the groups SO(3) and SU(2), and we will develop the relevant aspects of these groups and their matrix representations along the way. Students who would like to acquire a deeper understanding of groups and their representations from a physics perspective should consult the excellent texts by Barut and Raczka [2] or Cornwell [6] for groups in general, or Sexl and Urbantke [37] for emphasis on the Poincaré and Lorentz groups. However, this is not required for understanding the following chapters.

7.3 Operators for kinetic energy and angular momentum

The kinetic operator in spherical coordinates follows from (5.25) as

$$\begin{aligned}\frac{\mathbf{p}^2}{2\mu}&=-\frac{\hbar^2}{2\mu}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2}\frac{\partial^2}{\partial\vartheta^2}+\frac{\cot\vartheta}{r^2}\frac{\partial}{\partial\vartheta}+\frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\langle\boldsymbol{r}|\\&=-\frac{\hbar^2}{2\mu}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\frac{1}{r}\frac{\partial^2}{\partial r^2}r\langle\boldsymbol{r}|+\frac{\boldsymbol{M}^2}{2\mu r^2},\end{aligned}$$

where $\boldsymbol{M}$ is the angular momentum operator

$$\boldsymbol{M}=\mathbf{r}\times\mathbf{p}=\frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\boldsymbol{r}\times\nabla\langle\boldsymbol{r}|$$

$$
\begin{aligned}
&= \frac{\hbar}{\mathrm{i}} \int d^3\boldsymbol{r}\, |\boldsymbol{r}\rangle \left(\boldsymbol{e}_\varphi \frac{\partial}{\partial \vartheta} - \frac{1}{\sin \vartheta} \boldsymbol{e}_\vartheta \frac{\partial}{\partial \varphi} \right) \langle \boldsymbol{r}| \\
&= \frac{\hbar}{\mathrm{i}} \int d^3\boldsymbol{r}\, |\boldsymbol{r}\rangle \left[\boldsymbol{e}_x \left(-\sin\varphi \frac{\partial}{\partial \vartheta} - \cot\vartheta \cdot \cos\varphi \frac{\partial}{\partial \varphi} \right) \right. \\
&\quad \left. + \boldsymbol{e}_y \left(\cos\varphi \frac{\partial}{\partial \vartheta} - \cot\vartheta \cdot \sin\varphi \frac{\partial}{\partial \varphi} \right) + \boldsymbol{e}_z \frac{\partial}{\partial \varphi} \right] \langle \boldsymbol{r}|. \qquad (7.10)
\end{aligned}
$$

The property

$$
\boldsymbol{M}^2 = -\hbar^2 \int d^3\boldsymbol{r}\, |\boldsymbol{r}\rangle \left(\frac{\partial^2}{\partial \vartheta^2} + \cot\vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial \varphi^2} \right) \langle \boldsymbol{r}| \qquad (7.11)
$$

follows from

$$
\partial_\varphi \boldsymbol{e}_\varphi = -\cos\varphi\, \boldsymbol{e}_x - \sin\varphi\, \boldsymbol{e}_y = -\sin\vartheta\, \boldsymbol{e}_r - \cos\vartheta\, \boldsymbol{e}_\vartheta .
$$

The energy eigenvalue problem for the relative motion therefore reads

$$
\left(-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + V(r) \right) \langle \boldsymbol{r}|\psi\rangle + \frac{1}{2\mu r^2} \langle \boldsymbol{r}|\boldsymbol{M}^2|\psi\rangle = E\langle \boldsymbol{r}|\psi\rangle, \qquad (7.12)
$$

and we can deal with the angular part in the equation by first solving the eigenvalue problem for the operator $\boldsymbol{M}^2$.

A useful tool for the analysis of angular momentum operators is the ϵ *tensor* or *Eddington tensor*. The ϵ tensor in an n-dimensional flat space is the completely anti-symmetric tensor of n-th order

$$
\epsilon_{i_1 i_2 \ldots i_{k-1} i_k i_{k+1} \ldots i_{m-1} i_m i_{m+1} \ldots i_{n-1} i_n} = -\epsilon_{i_1 i_2 \ldots i_{k-1} i_m i_{k+1} \ldots i_{m-1} i_k i_{m+1} \ldots i_{n-1} i_n}
$$

with the normalization

$$
\epsilon_{123\ldots n} = 1.
$$

This tensor has n^n components. Anti-symmetry and the normalization imply that $n!/2$ of the components have the value 1, $n!/2$ of the components have the value -1, and $n^n - n!$ components vanish. We often use the ϵ tensor in three dimensions,

$$
\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = -\epsilon_{213} = -\epsilon_{132} = -\epsilon_{321} = 1.
$$

This tensor appears e.g. if we express cross products of vectors in terms of their components in a Cartesian basis $\boldsymbol{e}_i$,

$$
\boldsymbol{a} = a_i \boldsymbol{e}_i, \quad \boldsymbol{b} = b_i \boldsymbol{e}_i \quad \Rightarrow \quad \boldsymbol{a} \times \boldsymbol{b} = \boldsymbol{e}_i \epsilon_{ijk} a_j b_k. \qquad (7.13)
$$

This relation can be verified directly from the explicit definition of cross products like $(\boldsymbol{a}\times\boldsymbol{b})_1 = a_2b_3 - a_3b_2$ etc., or it can be considered as a consequence of a relation for the cross product of Cartesian basis vectors,

$$\boldsymbol{e}_i \times \boldsymbol{e}_j = \epsilon_{ijk}\boldsymbol{e}_k.$$

An example of (7.13) which involves the gradient operator is the curl of a vector field,

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} = \boldsymbol{e}_i\epsilon_{ijk}\partial_j A_k.$$

A useful identity is

$$\epsilon_{ijk}\epsilon_{k\ell m} = \delta_{i\ell}\delta_{jm} - \delta_{im}\delta_{j\ell}. \tag{7.14}$$

This identity yields e.g. the relations

$$\boldsymbol{a}\times(\boldsymbol{b}\times\boldsymbol{c}) = (\boldsymbol{a}\cdot\boldsymbol{c})\boldsymbol{b} - (\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{c},$$
$$\nabla\times(\nabla\times\boldsymbol{A}) = \nabla(\nabla\cdot\boldsymbol{A}) - \Delta\boldsymbol{A}.$$

Equation (7.13) implies that the Cartesian components of the angular momentum operator are related to the Cartesian components of position and momentum operators according to

$$M_i = \epsilon_{ijk}\mathrm{x}_j\mathrm{p}_k = \frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\epsilon_{ijk}x_j\frac{\partial}{\partial x^k}\langle\boldsymbol{r}|.$$

The first of these relations and the canonical commutation relations $[\mathrm{x}_i, \mathrm{p}_j] = \mathrm{i}\hbar\delta_{ij}$ imply the angular momentum commutation relations

$$[M_i, M_j] = \mathrm{i}\hbar\epsilon_{ijk}M_k. \tag{7.15}$$

Determination of the eigenvalues of $\boldsymbol{M}^2$ is equivalent to the determination of all hermitian matrix representations of the Lie algebra (7.15), which in turn is equivalent to the determination of all the matrix representations of the rotation group. We will find that all those matrix representations are realized in rotationally symmetric quantum systems. Therefore our next task is the determination of all the matrix representations of (7.15).

7.4 Matrix representations of the rotation group

We will start the study of matrix representations of the rotation group by looking at the defining representation, and then derive the general matrix representation.

The defining representation of the three-dimensional rotation group

In Section 4.1 we found the condition

$$\underline{R}\cdot\underline{R}^T = \underline{1}$$

for rotation matrices. This leaves the following possibilities for the matrix[1] $\underline{X} = \ln\underline{R}$,

$$\underline{X}^T = -\underline{X} + 2\pi \mathrm{i} n\underline{1}. \tag{7.16}$$

The equation

$$\det(\exp\underline{X}) = \exp(\mathrm{tr}\underline{X}), \tag{7.17}$$

which follows from the existence of a Jordan canonical form (F.2) for every matrix, implies then

$$\det\underline{R} = \exp\left(\mathrm{tr}\,\frac{\underline{X}+\underline{X}^T}{2}\right) = (-1)^n,$$

i.e. $\det\underline{R} = \pm 1$. Pure rotations have $\det\underline{R} = 1$, whereas additional inversion of an odd number of axes[2] yields $\det\underline{R} = -1$. We will focus on pure rotations.

The general solution of equation (7.16) in three dimensions and with $n = 0$ is

$$\underline{X} = \begin{pmatrix} 0 & \varphi_3 & -\varphi_2 \\ -\varphi_3 & 0 & \varphi_1 \\ \varphi_2 & -\varphi_1 & 0 \end{pmatrix} = \varphi_i\underline{L}_i = \boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}},$$

where the basis of anti-symmetric real 3×3 matrices

$$\underline{L}_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \underline{L}_2 = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \underline{L}_3 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{7.18}$$

was introduced. We can write the equations above in short form $(\underline{L}_i)_{jk} = \epsilon_{ijk}$. The general orientation preserving rotation in three dimensions therefore has the form

$$\underline{R}(\boldsymbol{\varphi}) = \exp(\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}}).$$

---

[1] See Appendix F for the calculation of the logarithm of an invertible matrix.

[2] Inversion of three axes is equivalent to inversion of one axis combined with a rotation.

Expansion of the exponential function and ordering into even and odd powers of $\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}}$ yields the representation

$$\underline{R}(\boldsymbol{\varphi}) = \hat{\boldsymbol{\varphi}}\otimes\hat{\boldsymbol{\varphi}}^T + \left(\underline{1} - \hat{\boldsymbol{\varphi}}\otimes\hat{\boldsymbol{\varphi}}^T\right)\cos\varphi + \hat{\boldsymbol{\varphi}}\cdot\underline{\boldsymbol{L}}\sin\varphi. \tag{7.19}$$

Application of the matrix $\hat{\boldsymbol{\varphi}}\cdot\underline{\boldsymbol{L}}$ on a vector $\boldsymbol{r}$ generates a vector product,

$$(\hat{\boldsymbol{\varphi}}\cdot\underline{\boldsymbol{L}})\cdot\boldsymbol{r} = -\hat{\boldsymbol{\varphi}}\times\boldsymbol{r},$$

i.e. for every vector $\boldsymbol{r}$, the first term in (7.19) preserves the part $\boldsymbol{r}_\parallel = \hat{\boldsymbol{\varphi}}\otimes\hat{\boldsymbol{\varphi}}^T\cdot\boldsymbol{r}$ of the vector which is parallel to the vector $\boldsymbol{\varphi}$, the second term multiplies the orthogonal part $\boldsymbol{r}_\perp = \boldsymbol{r} - \boldsymbol{r}_\parallel$ by the factor $\cos\varphi$, and the third part takes the orthogonal part, rotates it by $\pi/2$ and multiplies it by the factor $\sin\varphi$,

$$\underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{r} = \boldsymbol{r}_\parallel + \boldsymbol{r}_\perp\cos\varphi - \hat{\boldsymbol{\varphi}}\times\boldsymbol{r}\sin\varphi.$$

This also implies that the direction $\hat{\boldsymbol{\varphi}}$ of the vector $\boldsymbol{\varphi}$ is the direction of the axis of rotation.

Exponentiation of the linear combinations $\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}}$ of the matrices (7.18) thus generates rotations in three dimensions, and therefore these matrices are also denoted as three-dimensional representations of *generators* of the rotation group. They satisfy the commutation relations

$$[\underline{L}_i, \underline{L}_j] = -\epsilon_{ijk}\underline{L}_k. \tag{7.20}$$

We will also use the hermitian matrices

$$\underline{M}_i = -\mathrm{i}\hbar\underline{L}_i, \quad [\underline{M}_i, \underline{M}_j] = \mathrm{i}\hbar\epsilon_{ijk}\underline{M}_k, \quad [\underline{M}_i, \underline{\boldsymbol{M}}^2] = 0. \tag{7.21}$$

It is no coincidence that the angular momentum operators

$$M_i = \epsilon_{ijk}\mathrm{x}_j\mathrm{p}_k$$

satisfy the same commutation relations. We will see that angular momentum operators also generate rotations, and a set of operators M_i generates rotations if and only if the operators satisfy the commutation relations (7.21). It is a consequence of the general Baker-Campbell-Hausdorff formula in Appendix E that the combination of any two rotations to a new rotation is completely determined by the commutation relations (7.21) of the generators of rotations.

The general matrix representations of the rotation group

We wish to classify all possible representations of the commutation relations (7.21) in vector spaces. To accomplish this, it is convenient to change the basis from $M_x \equiv$

M_1 and $M_y \equiv M_2$ to

$$M_{\pm} = M_1 \pm \mathrm{i}M_2, \quad M_z \equiv M_3.$$

The product $\boldsymbol{M}^2 \equiv M_i M_i$ is then

$$\boldsymbol{M}^2 = \frac{1}{2}(M_+M_- + M_-M_+) + M_z{}^2 = M_-M_+ + M_z{}^2 + \hbar M_z,$$

and we have the commutation relations in the new basis,

$$[M_z, M_{\pm}] = \pm\hbar M_{\pm}, \quad [M_+, M_-] = 2\hbar M_z.$$

Hermiticity[3] implies that we can use a basis where M_z is diagonal with real eigenvalues,

$$M_z|m\rangle = \hbar m|m\rangle, \quad m \in \mathbb{R}.$$

The commutation relations then imply

$$\begin{aligned} &M_{\pm}|m\rangle = \hbar C_{\pm}(m)|m \pm 1\rangle, \\ &C_+(m-1)C_-(m) = 2\hbar m + C_-(m+1)C_+(m), \end{aligned} \tag{7.22}$$

and $M_+{}^+ = M_-$ implies

$$C_-(m) = \langle m-1|M_-|m\rangle = (\langle m|M_+{}^+|m-1\rangle)^+ = C_+(m-1)^+.$$

Substitution in equation (7.22) yields

$$|C_+(m)|^2 = |C_+(m-1)|^2 - 2\hbar^2 m.$$

Since the left hand side cannot become negative, there must exist some maximal value ℓ for m such that $C_+(\ell) = 0$, $M_+|\ell\rangle = 0$, and we have

$$|C_+(\ell-1)|^2 = 2\hbar^2\ell, \quad |C_+(\ell-2)|^2 = 2\hbar^2(2\ell-1),$$

and after $n-1$ steps

$$|C_+(\ell-n)|^2 = |C_-(\ell-n+1)|^2 = \hbar^2[2n\ell - n(n-1)]. \tag{7.23}$$

Again, the left hand side cannot become negative, and therefore the expression on the right hand side must terminate for some value N of n, $C_-(\ell-N+1) = 0$, $M_-|\ell-N+1\rangle = 0$. This implies existence of an integer N such that $2\ell = N-1$ and

$$C_+(\ell-N) = C_+(-(N+1)/2) = C_-((1-N)/2) = C_-(-\ell) = 0, \tag{7.24}$$

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[3] We could do the following calculations in slightly more general form without using hermiticity, and then find hermiticity of the finite-dimensional representations along the way.

where an irrelevant possible phase factor was excluded. Therefore we have boundaries

$$-\ell = \frac{1-N}{2} \leq m \leq \frac{N-1}{2} = \ell \tag{7.25}$$

and $N = 2\ell + 1$ possible values for m both for integer ℓ and half-integer ℓ.

Equation (7.23) yields with

$$n = \frac{N-1}{2} - m$$

the equation

$$\begin{aligned} n(N-n) &= \frac{N^2}{4} - \left(m + \frac{1}{2}\right)^2 = \frac{N^2-1}{4} - m(m+1) \\ &= \ell(\ell+1) - m(m+1), \end{aligned}$$

and therefore

$$\begin{aligned} C_+(m)^2 &= \hbar^2 \left(\frac{N^2-1}{4} - m(m+1)\right) = \hbar^2 \left[\ell(\ell+1) - m(m+1)\right], \\ C_-(m)^2 &= C_+(m-1)^2 = \hbar^2 \left[\ell(\ell+1) - m(m-1)\right]. \end{aligned}$$

We have found all the hermitian matrix representations of the commutation relations (7.21). The magnetic quantum number m can take values $-\ell \leq m \leq \ell$, the number of dimensions is $N = 2\ell + 1 \in \mathbb{N}$, and the actions of the angular momentum operators are

$$M_z|\ell, m\rangle = \hbar m|\ell, m\rangle, \quad 2\ell \in \mathbb{N}_0, \quad m \in \{-\ell, -\ell+1, \ldots, \ell-1, \ell\}, \tag{7.26}$$

$$M_+|\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \tag{7.27}$$

$$M_-|\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle \tag{7.28}$$

$$\begin{aligned} M_x|\ell, m\rangle &= \frac{\hbar}{2}\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \\ &\quad + \frac{\hbar}{2}\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle, \end{aligned} \tag{7.29}$$

$$\begin{aligned} M_y|\ell, m\rangle &= \frac{\hbar}{2\mathrm{i}}\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \\ &\quad - \frac{\hbar}{2\mathrm{i}}\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle, \end{aligned} \tag{7.30}$$

$$\boldsymbol{M}^2|\ell, m\rangle = \left(C_+(\ell, m)^2 + \hbar^2 m(m+1)\right)|\ell, m\rangle = \hbar^2\ell(\ell+1)|\ell, m\rangle. \tag{7.31}$$

7.5 Construction of the spherical harmonic functions

We now want to construct the $\boldsymbol{r}$ representations of the angular momentum eigenstates $|\ell, m\rangle$, i.e. we are seeking the solutions $\langle\vartheta, \varphi|\ell, m\rangle \equiv Y_{\ell,m}(\vartheta, \varphi)$ of the differential equations

$$\begin{aligned}\langle\vartheta, \varphi|\boldsymbol{M}^2|\ell, m\rangle &\equiv -\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)Y_{\ell,m}(\vartheta, \varphi)\\ &= \hbar^2\ell(\ell+1)Y_{\ell,m}(\vartheta, \varphi)\end{aligned}$$

and

$$\langle\vartheta, \varphi|M_z|\ell, m\rangle \equiv \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}Y_{\ell,m}(\vartheta, \varphi) = \hbar m Y_{\ell,m}(\vartheta, \varphi).$$

Here we used that the angular momentum operators act in $\boldsymbol{r}$ space as differential operators with respect to ϑ and φ, and therefore do not determine the radial dependence of wave functions. The radial part can therefore be left out in their representation[4],

$$\begin{aligned}\boldsymbol{M}^2 &= -\hbar^2\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\ \sin\vartheta\,|\vartheta, \varphi\rangle\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\langle\vartheta, \varphi|,\\ M_z &= \frac{\hbar}{\mathrm{i}}\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\ \sin\vartheta\,|\vartheta, \varphi\rangle\frac{\partial}{\partial\varphi}\langle\vartheta, \varphi|,\\ M_+ &= \hbar\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\ \sin\vartheta\,|\vartheta, \varphi\rangle\exp(\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi} + \frac{\partial}{\partial\vartheta}\right)\langle\vartheta, \varphi|,\\ M_- &= \hbar\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\ \sin\vartheta\,|\vartheta, \varphi\rangle\exp(-\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi} - \frac{\partial}{\partial\vartheta}\right)\langle\vartheta, \varphi|.\end{aligned}$$

The equation

$$\langle\vartheta, \varphi|M_z|\ell, \ell\rangle = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}\langle\vartheta, \varphi|\ell, \ell\rangle = \hbar\ell\langle\vartheta, \varphi|\ell, \ell\rangle \tag{7.32}$$

implies

$$\langle\vartheta, \varphi|\ell, \ell\rangle = Y_{\ell,\ell}(\vartheta, \varphi) = f_\ell(\vartheta)\exp(\mathrm{i}\ell\varphi).$$

Single valuedness of the eigenstates implies $\ell \in \mathbb{N}_0$.

The equation

$$\langle\vartheta, \varphi|M_+|\ell, \ell\rangle = \hbar\exp(\mathrm{i}\varphi)\left(\frac{\partial}{\partial\vartheta} + \mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi}\right)\langle\vartheta, \varphi|\ell, \ell\rangle = 0 \tag{7.33}$$

---

[4] Stated differently, we leave out a factor $1 = \int_0^\infty drr^2|r\rangle\langle r|$.

implies

$$\left(\frac{\partial}{\partial\vartheta} - \ell\cot\vartheta\right) f_\ell(\vartheta) = 0,$$

with the solution $f_\ell(\vartheta) = N_\ell^{-1/2}\sin^\ell\vartheta$. The normalization constants are chosen to ensure

$$\int_0^\pi d\vartheta\, f_\ell^2(\vartheta)\sin\vartheta = 1.$$

They can be calculated recursively if we note that

$$N_0 = \int_0^\pi d\vartheta\ \sin\vartheta = 2$$

and

$$\begin{aligned}
N_{\ell\geq 1} &= \int_0^\pi d\vartheta\ \sin^{2\ell+1}\vartheta = \int_{-1}^1 d\xi\,(1-\xi^2)^\ell \\
&= \xi(1-\xi^2)^\ell\Big|_{-1}^1 + \int_{-1}^1 d\xi\, 2\ell\xi^2(1-\xi^2)^{\ell-1} \\
&= -2\ell N_\ell + 2\ell N_{\ell-1}.
\end{aligned}$$

This yields

$$\begin{aligned}
N_\ell &= \frac{2\ell}{2\ell+1}N_{\ell-1} = \frac{2^2\ell(\ell-1)}{(2\ell+1)(2\ell-1)}N_{\ell-2} = \ldots = \frac{2^\ell\ell!}{(2\ell+1)!!}2 \\
&= 2\frac{2^{2\ell}(\ell!)^2}{(2\ell+1)!},
\end{aligned}$$

and therefore

$$\langle\vartheta,\varphi|\ell,\ell\rangle = Y_{\ell,\ell}(\vartheta,\varphi) = \frac{(-)^\ell}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)!}{\pi}}\exp(\mathrm{i}\ell\varphi)\sin^\ell\vartheta. \tag{7.34}$$

We can get the other eigenfunctions from $\langle\vartheta,\varphi|\ell,\ell\rangle$ through repeated applications of the lowering operator M_-,

$$\begin{aligned}
Y_{\ell,m}(\vartheta,\varphi) &= \langle\vartheta,\varphi|\ell,m\rangle = \frac{\langle\vartheta,\varphi|M_-|\ell,m+1\rangle}{\hbar\sqrt{(\ell+m+1)(\ell-m)}} \\
&= \frac{\langle\vartheta,\varphi|(M_-)^2|\ell,m+2\rangle}{\hbar^2\sqrt{(\ell+m+1)(\ell+m+2)(\ell-m)(\ell-m-1)}} = \ldots \\
&= \frac{\langle\vartheta,\varphi|(M_-)^{\ell-m}|\ell,\ell\rangle}{\hbar^{\ell-m}}\,[(\ell+m+1)(\ell+m+2)\times\ldots\times 2\ell
\end{aligned}$$

$$\begin{aligned}&\times(\ell-m)(\ell-m-1)\times\ldots\times 1]^{-1/2}\\ &=\frac{1}{\hbar^{\ell-m}}\sqrt{\frac{(\ell+m)!}{(2\ell)!(\ell-m)!}}\langle\vartheta,\varphi|(M_-)^{\ell-m}|\ell,\ell\rangle\\ &=\sqrt{\frac{(\ell+m)!}{(2\ell)!\cdot(\ell-m)!}}\\ &\times\left[\exp(-\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi}-\frac{\partial}{\partial\vartheta}\right)\right]^{\ell-m}Y_{\ell,\ell}(\vartheta,\varphi).\end{aligned}\tag{7.35}$$

If we substitute $Y_{\ell,\ell}(\vartheta,\varphi)$ from (7.34) into (7.35), we find

$$\begin{aligned}Y_{\ell,m}(\vartheta,\varphi)&=\frac{(-)^m}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi)\\ &\times\left[\prod_{n=m+1}^{\ell}\left(n\cot\vartheta+\frac{d}{d\vartheta}\right)\right]\sin^\ell\vartheta\\ &=\frac{(-)^m}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi)\\ &\times\left[\prod_{n=m+1}^{\ell}\left(\sin^{-n}\vartheta\frac{d}{d\vartheta}\sin^n\vartheta\right)\right]\sin^\ell\vartheta\\ &=\frac{(-)^\ell}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi)\\ &\times\sin^{-m}\vartheta\frac{d^{\ell-m}}{d(\cos\vartheta)^{\ell-m}}\sin^{2\ell}\vartheta.\end{aligned}\tag{7.36}$$

Equations (7.35) or (7.36) provide a solution to the problem to construct the spherical harmonic functions. However, it is common to make the connection to orthogonal polynomials in the interval $[-1,1]$. If we use the following equation for the associated Legendre polynomials,

$$P_\ell^m(x)=(-)^m\frac{(\ell+m)!}{2^\ell\ell!\cdot(\ell-m)!}\left(1-x^2\right)^{-m/2}\frac{d^{\ell-m}}{dx^{\ell-m}}\left(x^2-1\right)^\ell,$$

we can also write

$$Y_{\ell,m}(\vartheta,\varphi)=(-)^m\sqrt{\frac{(2\ell+1)\cdot(\ell-m)!}{4\pi\cdot(\ell+m)!}}\exp(\mathrm{i}m\varphi)P_\ell^m(\cos\vartheta).\tag{7.37}$$

The identity

$$\left(x^2-1\right)^{m/2}\sqrt{\frac{(\ell-m)!}{(\ell+m)!}}\frac{d^{\ell+m}}{dx^{\ell+m}}\left(x^2-1\right)^{\ell}$$
$$=\left(x^2-1\right)^{-m/2}\sqrt{\frac{(\ell+m)!}{(\ell-m)!}}\frac{d^{\ell-m}}{dx^{\ell-m}}\left(x^2-1\right)^{\ell}$$

implies

$$Y_{\ell,-m}(\vartheta,\varphi)=(-)^m Y^{+}_{\ell,m}(\vartheta,\varphi).$$

The spherical harmonic functions provide an orthonormal basis for functions on the sphere. The completeness relations are

$$\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,Y_{\ell,m}(\vartheta,\varphi)Y^{+}_{\ell',m'}(\vartheta,\varphi)=\delta_{\ell,\ell'}\delta_{m,m'}\tag{7.38}$$

and

$$\begin{aligned}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}Y_{\ell,m}(\vartheta,\varphi)Y^{+}_{\ell,m}(\vartheta',\varphi')&=\delta(\hat{\boldsymbol{r}}-\hat{\boldsymbol{r}}')\\&=\delta(\cos\vartheta-\cos\vartheta')\delta(\varphi-\varphi').\end{aligned}\tag{7.39}$$

In bra-ket notation we can write these completeness relations for functions on the sphere as

$$\int_0^{\pi}d\vartheta\int_0^{2\pi}d\varphi\,\sin\vartheta\,|\vartheta,\varphi\rangle\langle\vartheta,\varphi|=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}|\ell,m\rangle\langle\ell,m|=1,\tag{7.40}$$

i.e. the spherical harmonics $Y_{\ell,m}(\vartheta,\varphi)=\langle\vartheta,\varphi|\ell,m\rangle$ discretize functions on the sphere in the same sense as the Fourier monomials discretize functions on a circle or a finite interval (Sec. 10.1 contains a brief review of Fourier monomials on a finite interval). Knowledge of a continuous function $\langle\vartheta,\varphi|f\rangle$ on the sphere is equivalent to knowing the enumerably many numbers $\langle\ell,m|f\rangle$.

The lowest order spherical harmonics are

$$Y_{0,0}(\vartheta,\varphi)=\frac{1}{\sqrt{4\pi}},\quad Y_{1,0}(\vartheta,\varphi)=\sqrt{\frac{3}{4\pi}}\cos\vartheta,$$
$$Y_{1,\pm1}(\vartheta,\varphi)=\mp\sqrt{\frac{3}{8\pi}}\exp(\pm\mathrm{i}\varphi)\sin\vartheta,\quad Y_{2,0}(\vartheta,\varphi)=\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\vartheta-1),$$

$$Y_{2,\pm 1}(\vartheta,\varphi) = \mp\frac{1}{4}\sqrt{\frac{30}{\pi}}\exp(\pm \mathrm{i}\varphi)\sin\vartheta\cos\vartheta,$$

$$Y_{2,\pm 2}(\vartheta,\varphi) = \frac{1}{8}\sqrt{\frac{30}{\pi}}\exp(\pm 2\mathrm{i}\varphi)\sin^2\vartheta.$$

7.6 Basic features of motion in central potentials

Separation of the wave function in equation (7.12)

$$\psi(\boldsymbol{r}) = \psi(r)Y_{\ell,m}(\vartheta,\varphi) \tag{7.41}$$

and use of

$$\boldsymbol{M}^2|\ell,m\rangle = \hbar^2\ell(\ell+1)|\ell,m\rangle$$

yields the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)\psi(r) = E\psi(r). \tag{7.42}$$

The effective potential for the radial part of the relative motion of the two particles is therefore

$$V_{\mathrm{eff}}(r) = V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2},$$

with a “centrifugal barrier” term $\boldsymbol{M}^2/(2\mu r^2)$ just like in classical mechanics. The reason for this term is essentially the same consistency requirement as in classical mechanics. Classically, two particles with non-vanishing relative angular momentum $\boldsymbol{M}$ can never be in the same location, and the centrifugal barrier term simply reflects this property. Quantum mechanically, non-vanishing relative angular momentum $\boldsymbol{M}$ implies that the particular value $\psi(r=0)$ of the radial wave function must be suppressed, and it must be more strongly suppressed for larger $\boldsymbol{M}^2$.

Equation (7.42) is usually solved by the Sommerfeld method. In the first step one studies the asymptotic equations for small r and for large r, and keeps only the normalizable solutions or those solutions which approximate Fourier monomials in the asymptotic regions. In the next step one makes an *ansatz* for the full solution by multiplying the asymptotic solutions with a polynomial. Before we apply this method to the hydrogen atom, we will do something that one might find odd at first sight. The simplest case of a radially symmetric potential is $V=0$, i.e. free motion. It is of interest both for scattering theory and for ionization or decay of rotationally symmetric systems to discuss free motion with defined angular momentum, when the wave function for a free particle has the form (7.41).

7.7 Free spherical waves: The free particle with sharp $M_z, \boldsymbol{M}^2$

The radial Schrödinger equation for a free particle with fixed angular momentum $M_z, \boldsymbol{M}^2$ and energy $E = \hbar^2 k^2/2\mu$ is

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\psi(r) = E\psi(r),$$

or

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) r\psi(r) = 0. \tag{7.43}$$

The regular solution for $\ell = 0$ is

$$\psi_{k,0}(r) = \sqrt{\frac{2}{\pi}}\frac{\sin(kr)}{kr},$$

where the pre-factor was determined from the normalization condition

$$\int_0^\infty dr\, r^2 \psi_{k,0}(r)\psi_{k',0}(r) = \frac{1}{kk'}\delta(k-k').$$

For the study of solutions $\psi_{k,\ell}(r)$ for higher ℓ, we observe that solutions of equation (7.43) for $kr \ll \sqrt{\ell(\ell+1)}$ are $\psi(r) \propto r^\ell$ or $\psi(r) \propto r^{-\ell-1}$. We will only study solutions which are regular for $r = 0$, i.e. for $kr \ll \sqrt{\ell(\ell+1)}$ our solutions must approximate r^ℓ. Therefore we substitute $\psi_{k,\ell}(r) = r^\ell f_{k,\ell}(r)$ into equation (7.43),

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}(\ell+1)\frac{d}{dr} + k^2\right) f_{k,\ell}(r) = \left(\frac{1}{r}\frac{d^2}{dr^2}r + \frac{2\ell}{r}\frac{d}{dr} + k^2\right) f_{k,\ell}(r) = 0.$$

It is useful to write this as

$$\left(A_r B_r + 2\ell A_r + k^2\right) f_{k,\ell}(r) = 0 \tag{7.44}$$

with operators

$$A_r = \frac{1}{r}\frac{d}{dr}, \quad B_r = \frac{d}{dr}r.$$

These operators satisfy the commutation relation

$$[A_r, B_r] = 2A_r,$$

and this implies

$$\begin{aligned} A_r\left(A_r B_r + k^2\right) &= A_r\left(B_r A_r + 2A_r + k^2\right) = \left(A_r B_r + 2A_r + k^2\right) A_r, \\ A_r^\ell\left(A_r B_r + k^2\right) &= \left(A_r B_r + 2\ell A_r + k^2\right) A_r^\ell. \end{aligned} \tag{7.45}$$

This yields

$$f_{k,\ell}(r) \propto \frac{1}{r}\frac{d}{dr}f_{k,\ell-1}(r) \propto \left(\frac{1}{r}\frac{d}{dr}\right)^{\ell} f_{k,0}(r) = \sqrt{\frac{2}{\pi}}\left(\frac{1}{r}\frac{d}{dr}\right)^{\ell}\frac{\sin(kr)}{kr}, \tag{7.46}$$

$$\psi_{k,\ell}(r) \propto \sqrt{\frac{2}{\pi}}r^{\ell}\left(\frac{1}{r}\frac{d}{dr}\right)^{\ell}\frac{\sin(kr)}{kr} = (-)^{\ell}k^{\ell}\sqrt{\frac{2}{\pi}}j_{\ell}(kr). \tag{7.47}$$

Here we used the definition of the spherical Bessel functions

$$j_{\ell}(x) = (-x)^{\ell}\left(\frac{1}{x}\frac{d}{dx}\right)^{\ell}\frac{\sin x}{x} = \sqrt{\frac{\pi}{2x}}J_{\ell+\frac{1}{2}}(x).$$

The asymptotic expansion of $j_{\ell}(x)$ is

$$j_{\ell}(x)\Big|_{x\gg 1} \approx \frac{1}{x}\sin\left(x - \frac{\pi\ell}{2}\right).$$

Therefore the properly normalized radial eigenfunctions are

$$\psi_{k,\ell}(r) = \sqrt{\frac{2}{\pi}}\mathrm{i}^{\ell}j_{\ell}(kr) = \sqrt{\frac{2}{\pi}}\left(\frac{r}{\mathrm{i}k}\right)^{\ell}\left(\frac{1}{r}\frac{d}{dr}\right)^{\ell}\frac{\sin(kr)}{kr}, \tag{7.48}$$

and the free spherical waves with sharp angular momenta $\boldsymbol{M}^2$, M_z are

$$\langle \boldsymbol{r}|k,\ell,m\rangle = \sqrt{\frac{2}{\pi}}\mathrm{i}^{\ell}j_{\ell}(kr)Y_{\ell,m}(\vartheta,\varphi) = \frac{\mathrm{i}^{\ell}}{\sqrt{kr}}J_{\ell+\frac{1}{2}}(kr)Y_{\ell,m}(\vartheta,\varphi). \tag{7.49}$$

Our conventions for the phase and the normalization of the radial wave function are motivated by the expansion of plane waves in terms of spherical harmonics. If we define

$$\langle \boldsymbol{k}|k',\ell,m\rangle = \frac{1}{kk'}\delta(k-k')Y_{\ell,m}(\hat{\boldsymbol{k}}),$$

we automatically get the expansion of plane waves in terms of spherical harmonics,

$$\begin{aligned}\langle \boldsymbol{r}|\boldsymbol{k}\rangle &= \frac{1}{\sqrt{2\pi}^3}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = \sqrt{\frac{2}{\pi}}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\mathrm{i}^{\ell}j_{\ell}(kr)Y_{\ell,m}(\hat{\boldsymbol{r}})Y^{+}_{\ell,m}(\hat{\boldsymbol{k}}) \\ &= \frac{1}{\sqrt{kr}}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\mathrm{i}^{\ell}J_{\ell+\frac{1}{2}}(kr)Y_{\ell,m}(\hat{\boldsymbol{r}})Y^{+}_{\ell,m}(\hat{\boldsymbol{k}}).\end{aligned} \tag{7.50}$$

This expansion is also particularly useful for $\exp(\mathrm{i}kz)$. We have $P^m_{\ell}(1) = \delta_{m,0}$ and therefore $Y_{\ell,m}(\boldsymbol{e}_z) = Y_{\ell,m}(\vartheta = 0) = \sqrt{(2\ell+1)/4\pi}$. This yields

$$\exp(\mathrm{i}kz) = \sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^{\ell}j_{\ell}(kr)P_{\ell}(\cos\vartheta). \tag{7.51}$$

The radial wave functions (7.48) of the free spherical waves (7.49) satisfy completeness relations on the half-line

$$\int_0^\infty dr\, r^2\, \psi_{k,\ell}(r)\psi_{k',\ell}(r) = \frac{1}{k^2}\delta(k-k'),$$

$$\int_0^\infty dk\, k^2\, \psi_{k,\ell}(r)\psi_{k,\ell}(r') = \frac{1}{r^2}\delta(r-r'). \tag{7.52}$$

If our discussion above does not refer to motion of a single particle with mass μ, but to relative motion of two non-interacting particles at locations

$$\boldsymbol{x}_1 = \boldsymbol{R} + \frac{m_2}{m_1+m_2}\boldsymbol{r}, \quad \boldsymbol{x}_2 = \boldsymbol{R} - \frac{m_1}{m_1+m_2}\boldsymbol{r}$$

we can write a full two-particle wave function with sharp angular momentum quantum numbers for the relative motion as

$$\langle \boldsymbol{R}, \boldsymbol{r}|\boldsymbol{K}, k, \ell, m\rangle = \frac{\mathrm{i}^\ell}{2\pi^2}\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}) j_\ell(kr) Y_{\ell,m}(\hat{\boldsymbol{r}}),$$

or we could also require sharp angular momentum quantum numbers L, M for the center or mass motion[5],

$$\langle \boldsymbol{R}, \boldsymbol{r}|K, L, M, k, \ell, m\rangle = \frac{2}{\pi}\mathrm{i}^{L+\ell} j_L(KR) j_\ell(kr) Y_{L,M}(\hat{\boldsymbol{R}}) Y_{\ell,m}(\hat{\boldsymbol{r}}).$$

7.8 Bound energy eigenstates of the hydrogen atom

The solution for the hydrogen atom was reported by Schrödinger in 1926 in the same paper where he introduced the time-independent Schrödinger equation[6].

We recall that separation of the wave function in equation (7.12)

$$\psi(\boldsymbol{r}) = \psi(r) Y_{\ell,m}(\vartheta, \varphi) \tag{7.53}$$

and use of $\boldsymbol{M}^2|\ell, m\rangle = \hbar^2\ell(\ell+1)|\ell, m\rangle$ yields the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(r) = E\psi(r), \tag{7.54}$$

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[5] ...or we could use total angular momentum, i.e. quantum numbers $K, k, j \in \{|L-\ell|, \ldots, L+\ell\}, m_j = M+m, L, \ell$.

[6] E. Schrödinger, Annalen Phys. 384, 361 (1926).

where the attractive Coulomb potential between charges e and $-e$ has been inserted. This yields asymptotic equations for small r,

$$-r^2\frac{d^2}{dr^2}r\psi(r)+\ell(\ell+1)r\psi(r)=0, \tag{7.55}$$

and for large r,

$$-\frac{d^2}{dr^2}r\psi(r)=\frac{2\mu E}{\hbar^2}r\psi(r). \tag{7.56}$$

The Euler type differential equation (7.55) has basic solutions $r\psi(r)=Ar^{\ell+1}+Br^{-\ell}$, but with $\ell\geq 0$ only the first solution $r\psi(r)\propto r^{\ell+1}$ will yield a finite probability density $|\psi(\boldsymbol{r})|^2$ near the origin.

The normalizable solution of (7.56) for $E<0$ is

$$r\psi(r)\propto\exp\!\left(-\sqrt{-2\mu E}r/\hbar\right). \tag{7.57}$$

We combine the asymptotic solutions with a polynomial $w(r)=\sum_{\nu\geq 0}c_\nu r^\nu$,

$$r\psi(r)=r^{\ell+1}w(r)\exp(-\kappa r)\,,\quad \kappa=\sqrt{-2\mu E}r/\hbar.$$

Substitution in (7.54) yields the condition

$$r\frac{d^2}{dr^2}w(r)+2(\ell+1-\kappa r)\frac{d}{dr}w(r)+\left(\frac{\mu e^2}{2\pi\epsilon_0\hbar^2}-2\kappa(\ell+1)\right)w(r)=0,$$

which in turn yields a recursion relation for the coefficients in the polynomial $w(r)$,

$$c_{\nu+1}=c_\nu\frac{2\kappa(\nu+\ell+1)-\frac{\mu e^2}{2\pi\epsilon_0\hbar^2}}{(\nu+1)(\nu+2\ell+2)}. \tag{7.58}$$

Normalizability of the solution requires termination of the polynomial $w(r)$ with a maximal power $N\equiv\max(\nu)\geq 0$ of r, i.e. $c_{N+1}=0$ and therefore

$$\kappa\equiv\frac{\sqrt{-2\mu E}}{\hbar}=\frac{\mu e^2}{4\pi\epsilon_0\hbar^2(N+\ell+1)}. \tag{7.59}$$

This implies energy quantization for the bound states in the form

$$E_n=-\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2}=-\frac{\alpha^2}{2}\mu c^2\frac{1}{n^2} \tag{7.60}$$

with the principal quantum number $n\equiv N+\ell+1$. Note that $N\geq 0$ implies the relation $n\geq\ell+1$ between the principal and the magnetic quantum number.

We used the definition

$$\alpha=\frac{e^2}{4\pi\epsilon_0\hbar c}=7.29735\ldots\times 10^{-3}=\frac{1}{137.036\ldots}. \tag{7.61}$$

of Sommerfeld's *fine structure constant* in (7.60).

We will also use equation (7.59) in the form $\kappa = (na)^{-1}$ with the Bohr radius

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = \frac{\hbar}{\alpha\mu c}. \tag{7.62}$$

The recursion relation is then

$$c_{\nu+1} = c_\nu \frac{2}{na}\frac{\nu+\ell+1-n}{(\nu+1)(\nu+2\ell+2)}, \quad 0 \le \nu \le N \equiv n-\ell-1. \tag{7.63}$$

This defines all coefficients c_ν in $w(r)$ in terms of the coefficient c_0, which finally must be determined from normalization. The factor $2/na$ in the recursion relation will generate a power $(2/na)^\nu$ in c_ν, such that $w(r)$ will be a polynomial in $2r/na$. The factor $(\nu+1)^{-1}$ will generate a factor $1/\nu!$ in c_ν, and the factor $(\nu+\alpha)/(\nu+\beta)$ with $\alpha = \ell+1-n$, $\beta = 2\ell+2$ will finally yield a polynomial of the form

$$\begin{aligned} w(r) = c_0\Bigg[1 + \frac{\alpha}{\beta}\frac{2r}{na} + \frac{1}{2!}\frac{\alpha(\alpha+1)}{\beta(\beta+1)}\left(\frac{2r}{na}\right)^2 \\ + \frac{1}{3!}\frac{\alpha(\alpha+1)(\alpha+2)}{\beta(\beta+1)(\beta+2)}\left(\frac{2r}{na}\right)^3 + \ldots\Bigg] = c_0 \times {}_1F_1(\alpha;\beta;2r/na). \end{aligned}$$

As indicated in this equation, the series for $c_0 = 1$ defines the confluent hypergeometric function ${}_1F_1(\alpha;\beta;x) \equiv M(\alpha;\beta;x)$ (also known as Kummer's function [1]). For $-\alpha \in \mathbb{N}_0$ and $\beta \in \mathbb{N}$ this function can also be expressed as an associated Laguerre polynomial. The normalized radial wave functions can then be written as

$$\begin{aligned} \psi_{n,\ell}(r) &= \frac{2}{n^2}\sqrt{\frac{(n+\ell)!}{(n-\ell-1)!a^3}}\,\frac{{}_1F_1(-n+\ell+1;2\ell+2;2r/na)}{(2\ell+1)!} \\ &\quad\times\left(\frac{2r}{na}\right)^\ell \exp\left(-\frac{r}{na}\right) \\ &= \frac{2}{n^2}\sqrt{\frac{(n-\ell-1)!}{(n+\ell)!a^3}}\left(\frac{2r}{na}\right)^\ell L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na}\right)\exp\left(-\frac{r}{na}\right). \end{aligned} \tag{7.64}$$

Substitution of the explicit series representation for $w(r)$ shows that the radial wave functions are products of a polynomial in $2r/na$ of order $n-1$ with $n-\ell$ terms, multiplied with the exponential function $\exp(-r/na)$,

$$\begin{aligned} \psi_{n,\ell}(r) &= \frac{2}{n^2}(-)^\ell\sqrt{\frac{(n+\ell)!(n-\ell-1)!}{a^3}}\exp\left(-\frac{r}{na}\right) \\ &\quad\times\sum_{k=\ell}^{n-1}\frac{(-2r/na)^k}{(k-\ell)!(n-k-1)!(k+\ell+1)!}. \end{aligned} \tag{7.65}$$

The representation (7.64) in terms of the associated Laguerre polynomials differs from older textbook representations by a factor $(n+\ell)!$ due to the modern definition of the normalization of associated Laguerre polynomials,

$$\begin{aligned} L_n^m(x) &= \frac{(-)^m}{(n+m)!}\frac{d^m}{dx^m}\left(\exp(x)\frac{d^{n+m}}{dx^{n+m}}\left[x^{n+m}\exp(-x)\right]\right) \\ &= \frac{(m+n)!}{n!\cdot m!}\,{}_1F_1(-n;m+1;x), \end{aligned}$$

which is also used in symbolic calculation programs. The normalization follows from

$$\int_0^\infty dx\,\exp(-x)x^{m+1}[L_n^m(x)]^2 = (2n+m+1)\frac{(n+m)!}{n!}, \tag{7.66}$$

but their standard orthogonality relation is

$$\int_0^\infty dx\,\exp(-x)x^m L_n^m(x)L_{n'}^m(x) = \frac{(n+m)!}{n!}\delta_{n,n'}. \tag{7.67}$$

Since they appear as eigenstates of the hydrogen Hamiltonian, the normalized bound radial wave functions must satisfy the orthogonality relation

$$\int_0^\infty dr\,r^2\,\psi_{n,\ell}(r)\psi_{n',\ell}(r) = \delta_{n,n'}. \tag{7.68}$$

This implies that the associated Laguerre polynomials must also satisfy a peculiar additional orthogonality relation which generalizes (7.66),

$$\begin{aligned} &\int_0^\infty dx\,\exp\!\left(-\frac{(n+n'+m+1)x}{(2n+m+1)(2n'+m+1)}\right)x^{m+1}L_n^m\!\left(\frac{x}{2n+m+1}\right) \\ &\times L_{n'}^m\!\left(\frac{x}{2n'+m+1}\right) = (2n+m+1)^{m+3}\frac{(n+m)!}{n!}\delta_{n,n'}. \end{aligned} \tag{7.69}$$

Squares $\psi_{n,\ell}^2(r)$ of the radial wave functions are plotted for low lying values of n and ℓ in Figures 7.1–7.6.

For the meaning of the radial wave function, recall that the full three-dimensional wave function is

$$\psi_{n,\ell,m}(\boldsymbol{r}) = \psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi).$$

This implies that $\psi_{n,\ell}^2(r)$ is a radial profile of the probability density $|\psi_{n,\ell,m}(\boldsymbol{r})|^2$ to find the particle (or rather the quasiparticle which describes relative motion in the hydrogen atom) in the location $\boldsymbol{r}$, but note that in each particular direction (ϑ,φ) the

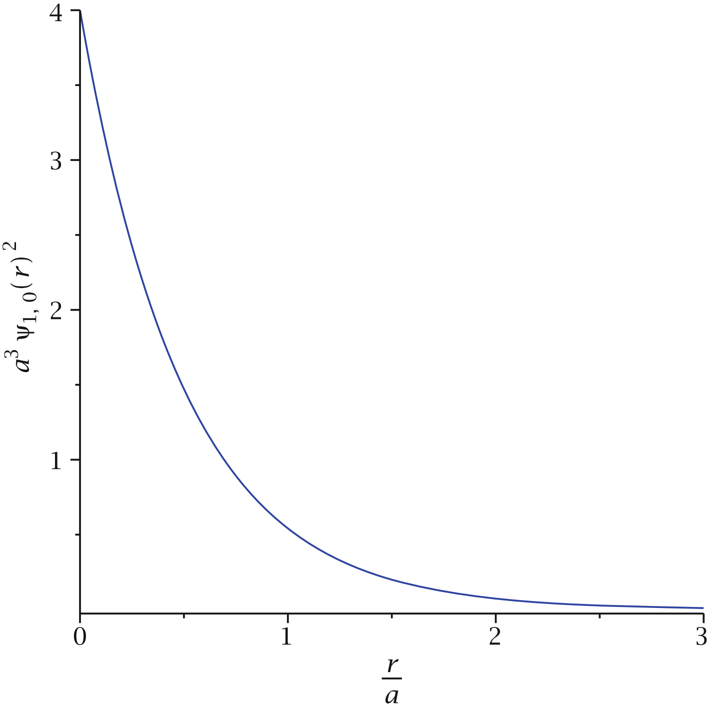

Fig. 7.1 The function $a^3\psi^2_{1,0}(r)$

radial profile is scaled by the factor $Y^2_{\ell,m}(\vartheta,\varphi)$ to give the actual radial profile of the probability density in that direction. Furthermore, note that the probability density for finding the electron-proton pair with separation between r and $r+dr$ is

$$\int_0^\pi d\vartheta \int_0^{2\pi} d\varphi\, r^2 \sin\vartheta\ |\psi_{n,\ell,m}(\boldsymbol{r})|^2 = r^2\psi^2_{n,\ell}(r).$$

The function $\psi^2_{n,\ell}(r)$ is proportional to the radial probability density in fixed directions, while $r^2\psi^2_{n,\ell}(r)$ samples the full spherical shell between r and $r+dr$ in all directions, and therefore the latter probability density is scaled by the geometric size factor r^2 for thin spherical shells.

Nowadays radial expectation values

$$\langle r^h\rangle_{n,\ell} = \int_0^\infty dr\, r^{h+2}\psi^2_{n,\ell}(r)$$

are readily calculated with symbolic computation programs. One finds in particular

$$\langle r\rangle_{n,\ell} = \frac{3n^2-\ell(\ell+1)}{2}a, \quad \langle r^2\rangle_{n,\ell} = \frac{n^2}{2}[5n^2+1-3\ell(\ell+1)]a^2.$$

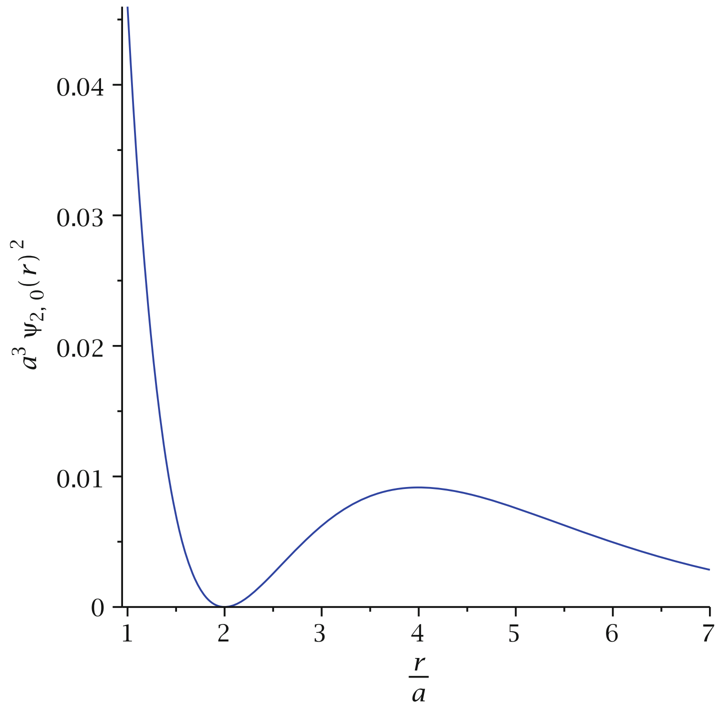

Fig. 7.2 The function $a^3\psi^2_{2,0}(r)$ for $r > a$

The resulting uncertainty in distance between the proton and the electron

$$(\Delta r)_{n,\ell} = \langle r^2\rangle_{n,\ell} - \langle r\rangle^2_{n,\ell} = \frac{a}{2}\sqrt{n^2(n^2+2) - \ell^2(\ell+1)^2}$$

is relatively large for most states in the sense that $(\Delta r/\langle r\rangle)_{n,\ell}$ is not small, except for large n states with large angular momentum. For example, we have $(\Delta r/\langle r\rangle)_{n,0} = \sqrt{1+(2/n^2)}/3 > 1/3$ but $(\Delta r/\langle r\rangle)_{n,n-1} = 1/\sqrt{2n+1}$. However, even for large n and ℓ, the particle could still have magnetic quantum number $m = 0$, whence its probability density would be uniformly spread over directions (ϑ, φ). This means that a hydrogen atom with sharp energy generically cannot be considered as consisting of a well localized electron near a well localized proton. This is just another illustration of the fact that simple particle pictures make no sense at the quantum level.

We also note from (7.64) or (7.65) that the bound eigenstates $\psi_{n,\ell,m}(\boldsymbol{r}) = \psi_{n,\ell}(r)Y_{\ell,m}(\vartheta, \varphi)$ have a typical linear scale

$$na = n\frac{4\pi\epsilon_0\hbar^2}{\mu Z e^2} \propto n\frac{\mu^{-1}}{Ze^2}. \tag{7.70}$$

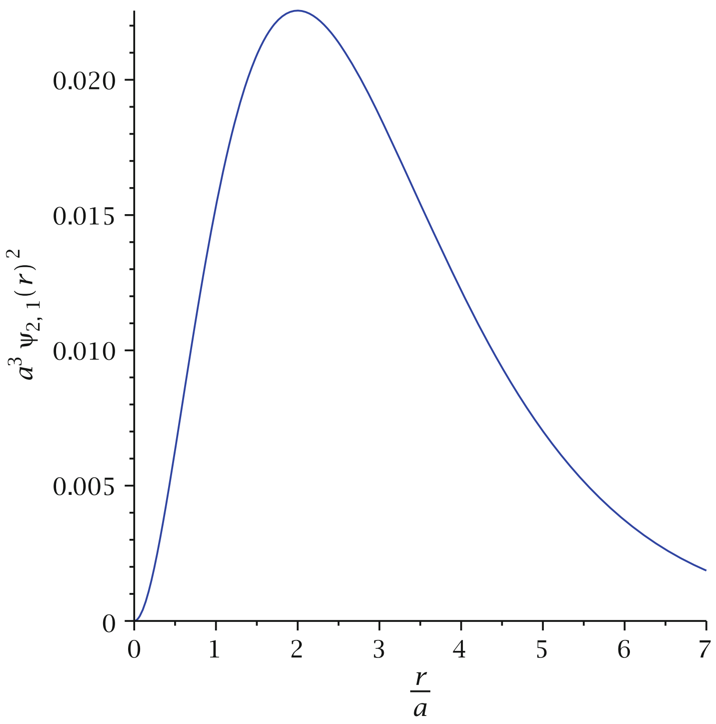

Fig. 7.3 The function $a^3\psi_{2,1}^2(r)$

Here we have generalized the definition of the Bohr radius a to the case of an electron in the field of a nucleus of charge Ze. Equation (7.70) is another example of the competition between the kinetic term $p^2/2\mu$ driving wave packets apart, and an attractive potential, here $V(r) = -Ze^2/4\pi\epsilon_0 r$, trying to collapse the wave function into a point. Metaphorically speaking, pressure from kinetic terms stabilizes the wave function. For given ratio of force constant Ze^2 and kinetic parameter μ^{-1} the attractive potential cannot compress the wave packet to sizes smaller than a, and therefore there is no way for the system to release any more energy. Superficially, there seems to exist a classical analog to the quantum mechanical competition between kinetic energy and attractive potentials in the Schrödinger equation. In classical mechanics, competition between centrifugal terms and attractive potentials can yield stable bound systems. However, the classical analogy is incomplete in a crucial point. The centrifugal term for $\ell \neq 0$ is also there in equation (7.54) exactly as in the classical Coulomb or Kepler problems. However, what stabilizes the wave function against core collapse in the crucial lowest energy case with $\ell = 0$ is the radial kinetic term, whereas in the classical case bound Coulomb or Kepler systems with vanishing angular momentum always collapse. To understand the quantum mechanical stabilization of atoms against collapse a little better, let us repeat equation (7.54) for $\ell = 0$ and nuclear charge Ze, and for low values of r,

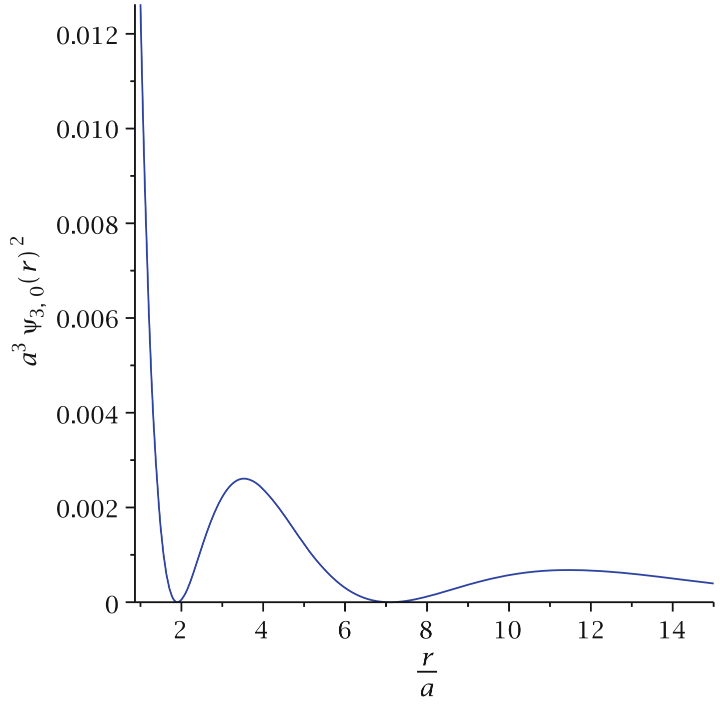

Fig. 7.4 The function $a^3\psi^2_{3,0}(r)$ for $r > a$

where we can assume $\psi(r) \neq 0$:

$$\frac{\hbar^2}{2\mu}\frac{1}{\psi(r)}\frac{d^2}{dr^2}r\psi(r) = -Er - \frac{Ze^2}{4\pi\epsilon_0}. \tag{7.71}$$

The radial probability amplitude $r\psi(r)$ must satisfy $\psi^{-1}(r)d^2(r\psi(r))/dr^2 < 0$ near the origin, to bend the function around to eventually yield $\lim_{r\to\infty} r\psi(r) = 0$, which is necessary for normalizability of $r^2\psi^2(r)$ on the half-axis $r > 0$. But near $r = 0$, the only term that bends the wave function in the right direction for normalizability is essentially the ratio Ze^2/μ^{-1},

$$\frac{1}{\psi(r)}\frac{d^2}{dr^2}r\psi(r) \simeq -\frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2}.$$

If we want to concentrate more and more of the wave function near the origin $r \simeq 0$, we have to bend it around already very close to $r = 0$ to reach small values $ar^2\psi^2(r) \ll 1$ very early. But the only parameter that bends the wave function near the origin $r \simeq 0$ is the ratio between attractive force constant and kinetic parameter, Ze^2/μ^{-1}. This limits the minimal spatial extension of the wave function

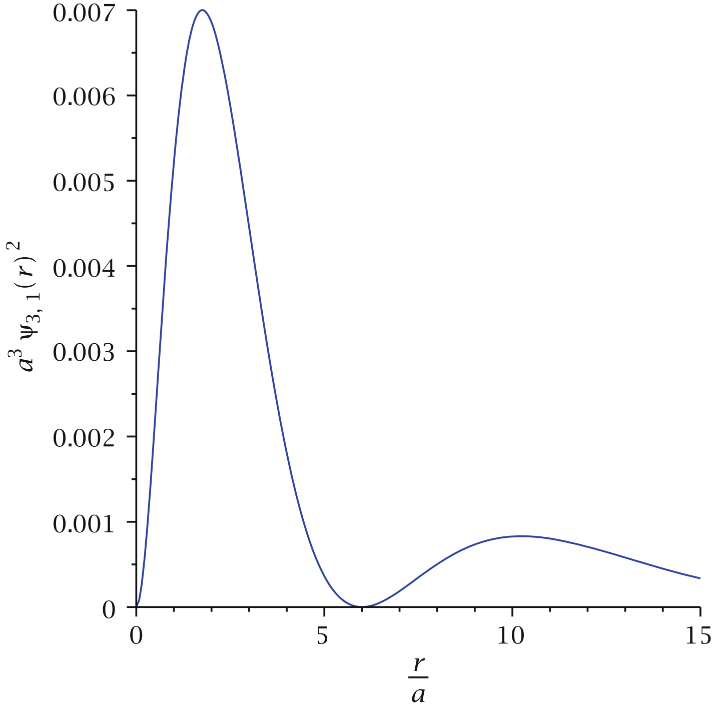

Fig. 7.5 The function $a^3\psi_{3,1}^2(r)$

and therefore prevents the classically inevitable core collapse in the bound Coulomb system with vanishing angular momentum $\boldsymbol{M} = \boldsymbol{0}$. In a nutshell, there is only so much squeezing of the wave function that Ze^2/μ^{-1} can do. See also Problem 7.15 for squeezing or stretching of a hydrogen atom near its ground state.

The radial probability amplitude $r\psi_{1,0}(r)$ for the ground state is plotted in Figure 7.7.

7.9 Spherical Coulomb waves

Now we assume $E > 0$. Recall that the asymptotic solutions for $r\psi(r)$ for $r \to 0$ were of the form $Ar^{\ell+1} + Br^{-\ell}$. Let us initially focus on the solutions which remain regular in the origin.

The symptotic behavior for large r *seems* to correspond to outgoing and incoming radial waves

$$r\psi_{\pm}(r) \to A_{\pm}\exp(\pm \mathrm{i}kr), \quad k = \sqrt{2\mu E}/\hbar.$$

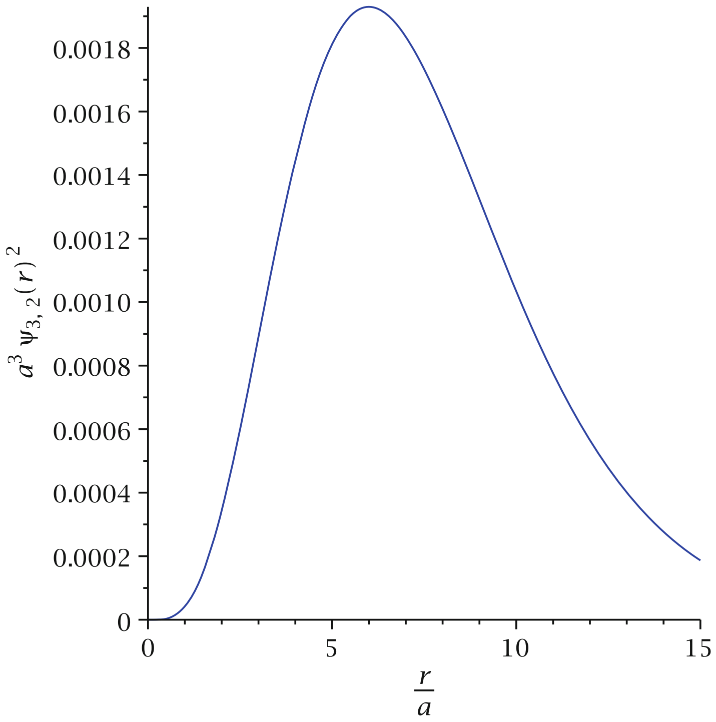

Fig. 7.6 The function $a^3\psi_{3,2}^2(r)$

Therefore we try an *ansatz*

$$r\psi_\pm(r) = w_\pm(r)r^{\ell+1}\exp(\pm\mathrm{i}kr), \quad w_\pm(r) = \sum_{\nu\geq 0} c_{\pm,\nu}r^\nu.$$

Instead of the recursion relation (7.58) we now find

$$c_{\pm,\nu+1} = -c_{\pm,\nu}\frac{2}{\nu+1}\frac{\frac{1}{a}\pm\mathrm{i}k(\nu+\ell+1)}{\nu+2\ell+2} \tag{7.72}$$

and therefore

$$\begin{aligned}w_\pm(r) \propto\ & 1 \mp \frac{\ell+1\mp\frac{\mathrm{i}}{ka}}{2\ell+2}2\mathrm{i}kr + \frac{\left(\ell+1\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+2\mp\frac{\mathrm{i}}{ka}\right)}{(2\ell+2)(2\ell+3)}\frac{(2\mathrm{i}kr)^2}{2!}\\ &\mp\frac{\left(\ell+1\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+2\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+3\mp\frac{\mathrm{i}}{ka}\right)}{(2\ell+2)(2\ell+3)(2\ell+4)}\frac{(2\mathrm{i}kr)^3}{3!}+\ldots\\ =\ & {}_1F_1(\ell+1\mp(\mathrm{i}/ka);2\ell+2;\mp 2\mathrm{i}kr).\end{aligned}$$

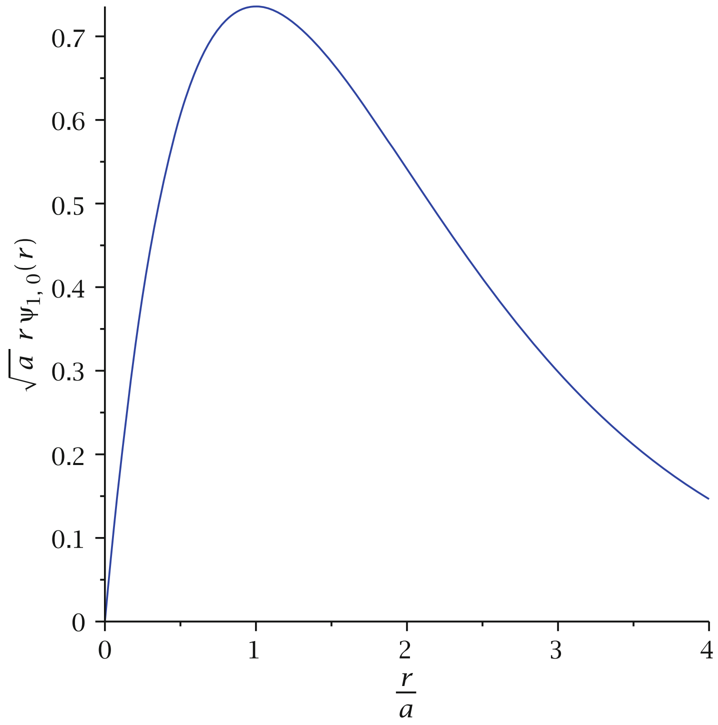

Fig. 7.7 The function $\sqrt{a}r\psi_{1,0}(r)$

However, the confluent hypergeometric function satisfies Kummer's identity

$$ {}_1F_1(\alpha;\beta;z) = \exp(z)\,{}_1F_1(\beta-\alpha;\beta;-z), $$

and this implies in particular

$$\begin{aligned} &\exp(\mathrm{i}kr)\,{}_1F_1(\ell+1-(\mathrm{i}/ka);2\ell+2;-2\mathrm{i}kr)\\ &\quad= \exp(-\mathrm{i}kr)\,{}_1F_1(\ell+1+(\mathrm{i}/ka);2\ell+2;2\mathrm{i}kr), \end{aligned}$$

i.e. there is only one regular solution for given quantum numbers (k,ℓ), and it corresponds neither to an outgoing nor to an incoming spherical wave, but is apparently rather a superposition of incoming and outgoing waves. For applications in scattering theory one often also has to look at solutions which are irregular in the origin,

$$ r\psi(r) = r^{-\ell}v_{\pm}(r)\exp(\pm\mathrm{i}kr), \quad v_{\pm}(r) = \sum_{\nu\geq 0} d_{\pm,\nu}r^{\nu}. $$

In this case, the radial Schrödinger equation yields

$$d_{\pm,\nu+1} = \mp d_{\pm,\nu}\frac{2\mathrm{i}k}{\nu+1}\frac{\nu-\ell\mp\frac{\mathrm{i}}{ka}}{\nu-2\ell}. \tag{7.73}$$

This recursion relation follows also directly from (7.72) with the substitution $\ell \to -\ell - 1$. The solution is

$$v_{\pm}(r) \propto {}_1F_1(-\ell \mp (\mathrm{i}/ka); -2\ell; \mp 2\mathrm{i}kr),$$

and we have again from Kummer's identity

$$\begin{aligned}&\exp(\mathrm{i}kr){}_1F_1(-\ell-(\mathrm{i}/ka);-2\ell;-2\mathrm{i}kr)\\&\quad=\exp(-\mathrm{i}kr){}_1F_1(-\ell+(\mathrm{i}/ka);-2\ell;2\mathrm{i}kr),\end{aligned}$$

i.e. there is also only one irregular solution for given quantum numbers (k,ℓ), as expected. Regular and irregular solutions can be combined to form outgoing or incoming spherical waves, see e.g. [1] or [28]. This is relevant when the long range Coulomb potential is combined with a short range scattering potential, because the short range part will modify the short distance properties of the states and both the regular and irregular spherical Coulomb waves are then needed to model the asymptotic behavior of incoming and scattered waves far from the short range scattering potential. This is relevant for scattering in nuclear physics, when short range scattering is effected by nuclear forces.

However, for us the regular solutions are more interesting because together with the bound states $\psi_{n,\ell,m}(\boldsymbol{r}) = \psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)$, the regular unbound states $\psi_{k,\ell,m}(\boldsymbol{r}) = \psi_{k,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)$ form a complete set in Hilbert space.

We use the normalization[7]

$$\begin{aligned}\psi_{k,\ell}(r) = {}&\sqrt{\frac{2}{\pi}}\exp\!\left(\frac{\pi}{2ak}\right)\frac{\left|\Gamma\!\left(\ell+1+\frac{\mathrm{i}}{ka}\right)\right|}{(2\ell+1)!}(2kr)^{\ell}\exp(-\mathrm{i}kr)\\&\times{}_1F_1(\ell+1+(\mathrm{i}/ka);2\ell+2;2\mathrm{i}kr).\end{aligned} \tag{7.74}$$

With this normalization the regular spherical Coulomb waves become the free waves with sharp angular momentum (7.48) in the limit of vanishing Coulomb potential $e^2 \to 0 \;\Rightarrow\; a \to \infty$, or if the energy $E = \hbar^2k^2/2\mu$ of the spherical Coulomb waves is much larger than the binding energy $E_B = -E_1 = \hbar^2/2\mu a^2$ of hydrogen, $E \gg E_B \;\Rightarrow\; ka \gg 1$.

Apart from the normalization, the spherical Coulomb waves $\psi_{k,\ell}(r)$ become the radial bound state wave functions $\psi_{n,\ell}(r)$ through the substitution $\mathrm{i}k \to (na)^{-1}$. This is expected since this substitution takes the positive energy Schrödinger equation into the negative energy Schrödinger equation.

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[7] W. Gordon, Annalen Phys. 394, 1031 (1929); M. Stobbe, Annalen Phys. 399, 661 (1930), see also [3]. Gordon and Stobbe normalized in the k scale, i.e. to $\delta(k-k')$ instead of $\delta(k-k')/k^2$.

The regular spherical Coulomb waves satisfy the orthogonality properties (cf. (7.68))

$$\int_0^\infty dr\, r^2\, \psi_{k,\ell}(r)\psi_{k',\ell}(r) = \frac{1}{k^2}\delta(k-k'), \quad \int_0^\infty dr\, r^2\, \psi_{k,\ell}(r)\psi_{n,\ell}(r) = 0,$$

and together with the radial bound state wave functions they satisfy the completeness relation[8]

$$\sum_{n=\ell+1}^{\infty} \psi_{n,\ell}(r)\psi_{n,\ell}(r') + \int_0^\infty dk\, k^2 \psi_{k,\ell}(r)\psi_{k,\ell}(r') = \frac{1}{r^2}\delta(r-r').$$

Together with the completeness relation (7.39) for the spherical harmonics, this implies completeness of the regular hydrogen states,

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty} \psi_{n,\ell,m}(\boldsymbol{r})\psi^+_{n,\ell,m}(\boldsymbol{r}') + \int_0^\infty dk\, k^2 \psi_{k,\ell,m}(\boldsymbol{r})\psi^+_{k,\ell,m}(\boldsymbol{r}')\right) = \delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{7.75}$$

For calculations of transitions between free and bound states, e.g. for electron-proton recombination cross sections, one needs free eigenstates which are not radially symmetric but approximate plane waves at large separations. To construct such a state from the spherical Coulomb waves, we can use that equation (7.51) tells us the decomposition of the plane wave exp(ikz) in terms of the free states of sharp angular momentum (7.48),

$$\exp(\mathrm{i}kz) = \sqrt{\frac{\pi}{2}}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\vartheta)\psi_{k,\ell}^{(e^2=0)}(r).$$

However, one needs to adjust the phase factors in the sum if one wants to get an asymptotic superposition of plane waves and outgoing spherical waves. The superposition of spherical Coulomb waves[9] (7.74),

$$\langle \boldsymbol{r}|\boldsymbol{k}\rangle_{MG} = \sqrt{\frac{\pi}{2}}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\vartheta)\frac{\Gamma\left(\ell+1+\frac{\mathrm{i}}{ka}\right)}{\left|\Gamma\left(\ell+1+\frac{\mathrm{i}}{ka}\right)\right|}\psi_{k,\ell}(r), \tag{7.76}$$

will correspond to a free energy eigenstate of hydrogen with energy $\hbar^2k^2/2\mu$ which up to logarithmic corrections approximates a superposition of a plane wave exp(ikz) with outgoing radial waves.

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[8] See e.g. N. Mukunda, Amer. J. Phys. 46, 910 (1978).

[9] N.F. Mott, Proc. Roy. Soc. London A 118, 542 (1928); W. Gordon, Z. Phys. 48, 180 (1928).

7.10 Problems

7.1. Show that the transformations (7.3, 7.4) imply

$$\boldsymbol{K}\cdot\boldsymbol{R}+\boldsymbol{k}\cdot\boldsymbol{r}=\boldsymbol{k}_1\cdot\boldsymbol{x}_1+\boldsymbol{k}_2\cdot\boldsymbol{x}_2. \tag{7.77}$$

What is then the proper boundary condition for $\lim_{r\to\infty}\psi(\boldsymbol{r})$ for an unbound 2-particle state of the form (7.7) if we assume that the two particles have asymptotic momenta $\hbar\boldsymbol{k}_1$ and $\hbar\boldsymbol{k}_2$ for large separation?

7.2. How large is the minimal value of the product $\Delta M_x \Delta M_y$ of uncertainties of angular momentum components in a state $|\ell, m_\ell\rangle$?

7.3. Why does equation (7.45) imply that there is no other choice but (7.46) for the regular solution $f_{k,\ell}(r)$ of (7.44)?

7.4. A simple spherical model for a color center or a quantum dot consists of an electron confined to a sphere of radius R. Inside the sphere the electron can move freely because the potential energy vanishes there, $V(r) = 0$ for $r < R$. The wave function in the sphere for given angular momentum quantum numbers will therefore have the form $\psi(\boldsymbol{r}) \propto j_\ell(kr)Y_{\ell,m}(\vartheta,\varphi)$.

Which energy quantization conditions will we get from the condition that the wave function vanishes for $r \geq R$? How large is the radius R if the electron absorbs photons of energy 2.3 eV?

Zeros $x_{n,\ell}$ of spherical Bessel functions, $j_\ell(x_{n,\ell}) = 0$, $n = 1, 2, \ldots$ can be found e.g. in Chapter 10 of [1].

Which relation between R and lattice constant d follows from Mollwo's relation $\nu d^2 = 5.02 \times 10^{-5}\,\mathrm{m}^2\,\mathrm{Hz}$?

In hindsight, color centers could be considered as the first realization of atomic scale quantum dots.

7.5. Show that the radial density profile $\psi^2_{n,\ell}(r)$ for bound states of hydrogen has maxima at the extrema of the radial wave function $\psi_{n,\ell}(r)$.

Remark. $\psi_{n,\ell}(r)$ and $d\psi_{n,\ell}(r)/dr$ have no common zeros, because this would contradict the radial Schrödinger equation.

7.6. Calculate the radius $r_{max}^{(n,n-1)}$ where the radial wave function $\psi_{n,n-1}(r)$ has a maximum. Compare your result to $\langle r\rangle_{n,n-1} \pm (\Delta r)_{n,n-1}$.

7.7. For $n \geq 2$ calculate the radius $r_{max}^{(n,n-2)}$ where the radial wave function $\psi_{n,n-2}(r)$ has a maximum.

7.8. As a rule of thumb, quantum systems tend to approach classical behavior for large quantum numbers. We have seen that for large quantum number n the radial wave function $\psi_{n,n-1}(r)$ is localized in a spherical shell $\langle r\rangle_{n,n-1} \pm (\Delta r)_{n,n-1}$ which is "thin" in the sense of $(\Delta r/\langle r\rangle)_{n,n-1} = 1/\sqrt{2n+1} \to 0$.

For sharp energy $E_{n,\ell,m}$, could we ever hope to find an approximately localized electron in a hydrogen atom?

7.9. Calculate the radial expectation values $\langle r^{-1}\rangle_{n,\ell}$, $\langle r^{-2}\rangle_{n,\ell}$ and $\langle r^{-3}\rangle_{n,\ell}$. These expectation values are relevant for interaction energies within the atom.

7.10. We have seen how the expectation value $\langle r\rangle$ for the separation between the electron and the proton depends on the quantum numbers n and ℓ. How large are the corresponding expectation values for the distances of the two particles from the center of mass of the hydrogen atom?

7.11. An electric field along the z axis shifts the potential energy of a hydrogen atom by a perturbation $\Delta V \propto z$. For which combinations of quantum numbers are the matrix elements $\langle n_1', n_2', m'|z|n_1, n_2, m\rangle$ different from zero?

7.12. Calculate the probability density to find the momentum $\boldsymbol{p}$ in the relative motion in a hydrogen atom in its ground state.

7.13. Calculate the probability densities to find the momentum $\boldsymbol{p}$ in the relative motion in a hydrogen atom for the $n = 2$ states $|2, \ell, m_\ell\rangle$.

7.14. We cannot construct energy eigenstates of the hydrogen atom which separate in the coordinates $\boldsymbol{x}_e$ and $\boldsymbol{x}_p$ of the electron and the proton. If we want to have a representation which factorizes in electron and proton wave functions, the best we can do is to expand the energy eigenstates $\Psi_{\boldsymbol{K},n,\ell,m}(\boldsymbol{R},\boldsymbol{r})$ in terms of complete sets of functions $f_e(\boldsymbol{x}_e)g_p(\boldsymbol{x}_p)$ which arise from complete sets of functions $f(\boldsymbol{x})$, $g(\boldsymbol{x})$ for single particle states. Expand the ground state of a hydrogen atom with center of mass momentum $\hbar\boldsymbol{K}$,

$$\Psi_{\boldsymbol{K},1,0,0}(\boldsymbol{R},\boldsymbol{r}) = \frac{1}{\sqrt{2a}^3\,\pi^2}\exp\!\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} - \frac{r}{a}\right)$$

in terms of the complete basis of factorized plane electron and proton waves,

$$\langle \boldsymbol{x}_e, \boldsymbol{x}_p|\boldsymbol{k}_e, \boldsymbol{k}_p\rangle = \frac{1}{(2\pi)^3}\exp\!\left(\mathrm{i}\boldsymbol{k}_e\cdot\boldsymbol{x}_e + \mathrm{i}\boldsymbol{k}_p\cdot\boldsymbol{x}_p\right).$$

Solution. Fourier transformation of

$$\langle \boldsymbol{x}_e, \boldsymbol{x}_p|1,0,0;\boldsymbol{K}\rangle = \frac{1}{\sqrt{2a}^3\,\pi^2}\exp\!\left(\mathrm{i}\boldsymbol{K}\cdot\frac{m_e\boldsymbol{x}_e + m_p\boldsymbol{x}_p}{m_e+m_p} - \frac{|\boldsymbol{x}_e - \boldsymbol{x}_p|}{a}\right)$$

yields

$$\begin{aligned}\langle \boldsymbol{k}_e, \boldsymbol{k}_p|1,0,0;\boldsymbol{K}\rangle &= \frac{\sqrt{2a}^3}{\pi}\delta(\boldsymbol{K} - \boldsymbol{k}_e - \boldsymbol{k}_p)\\ &\quad\times\left[1 + \frac{a^2}{(m_e+m_p)^2}\left|m_p\boldsymbol{k}_e - m_e\boldsymbol{k}_p\right|^2\right]^{-2}, \end{aligned} \tag{7.78}$$

i.e. the decomposition of the 1s hydrogen state with center of mass momentum $\hbar\boldsymbol{K}$ in terms of electron and proton plane wave states is

$$|1,0,0;\boldsymbol{K}\rangle = \frac{\sqrt{2a}^3}{\pi}\int d^3\boldsymbol{k}_e\,|\boldsymbol{k}_e\rangle\otimes|\boldsymbol{K}-\boldsymbol{k}_e\rangle \times\left[1+a^2\left|\boldsymbol{k}_e-\frac{m_e}{m_e+m_p}\boldsymbol{K}\right|^2\right]^{-2}. \tag{7.79}$$

Hint for the Fourier transformation: It is advantageous to use center of mass and relative coordinates for the calculation of the Fourier integrals, $d^3\boldsymbol{x}_e\wedge d^3\boldsymbol{x}_p = d^3\boldsymbol{r}\wedge d^3\boldsymbol{R}$.

7.15. Suppose we force a hydrogen atom into a 1s type state

$$\psi(\boldsymbol{r},t) = \frac{1}{\sqrt{\pi b^3}}\exp(-r/b)\exp(-\mathrm{i}E_1 t/\hbar), \tag{7.80}$$

where

$$E_1 = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a}$$

is the ground state energy of the hydrogen atom, but the length parameter b is *not* the Bohr radius a.

7.15a. How do the expectation values for kinetic, potential and total energy in the state (7.80) compare to the corresponding values in the ground state of the unperturbed hydrogen atom?

7.15b. How do we have to change the potential energy of the system to force the hydrogen atom into the state (7.80)? Show that the change in potential energy can be written as

$$\Delta V = \frac{\hbar^2}{\mu}\left(\frac{1}{a}-\frac{1}{b}\right)\left(\frac{1}{r}-\frac{1}{2a}-\frac{1}{2b}\right).$$

7.16. Solve the differential equation (6.6) for the harmonic oscillator not by the operator method, but by the same methods which we have used to solve the radial equation (7.54) for the hydrogen atom.

7.17. The proposal of Bohmian mechanics[10] asserts that quantum mechanics with the Born probability interpretation should be replaced by a pilot wave theory. The wave function would still satisfy the Schrödinger equation. However, instead of

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[10] D. Bohm, Phys. Rev. 85, 166 & 180 (1952).

serving as a probability amplitude for the outcome of single measurements, the wave function provides a pilot wave for particles in the sense that an N particle wave function determines the velocity field for the particles through the equation

$$\frac{d\boldsymbol{x}_I(t)}{dt} = \frac{\hbar}{2\mathrm{i}m_I\,|\psi(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)|^2} \times\left(\psi^+(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)\,\overset{\leftrightarrow}{\nabla}_I\,\psi(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)\right), \qquad (7.81)$$

where $\psi^+\,\overset{\leftrightarrow}{\nabla}\,\psi \equiv \psi^+\nabla\psi - (\nabla\psi^+)\psi$.

It has been claimed that this leads to predicitions which are indistinguishable from quantum mechanics, at least as long as we are only concerned with motion of non-relativistic particles.

We consider a hydrogen atom with center of mass velocity $\boldsymbol{V} = \hbar\boldsymbol{K}/(m_e + m_p)$. Which velocities would equation (7.81) predict for the velocities of the proton and the electron in the ground state of the atom? How would the proton and the electron then be arranged in the ground state of a hydrogen atom?

Solution. The ground state wave function in terms of electron and proton coordinates is

$$\langle\boldsymbol{x}_e,\boldsymbol{x}_p|1,0,0;\boldsymbol{K}(t)\rangle = \exp\!\left(\mathrm{i}\boldsymbol{K}\cdot\frac{m_e\boldsymbol{x}_e + m_p\boldsymbol{x}_p}{m_e+m_p}\right)\exp\!\left(-\frac{|\boldsymbol{x}_e-\boldsymbol{x}_p|}{a}\right) \times\frac{1}{\pi^2\sqrt{2a}^3}\exp\!\left(-\frac{\mathrm{i}\hbar}{2(m_e+m_p)}\boldsymbol{K}^2t - \frac{\mathrm{i}}{\hbar}E_1t\right).$$

Equation (7.81) then yields

$$\boldsymbol{v}_e = \boldsymbol{v}_p = \boldsymbol{V}.$$

This result agrees with the corresponding expectation values for particle velocities in quantum mechanics. However, here we assume that both the electron and the proton have well defined (although not individually observable) trajectories, and their velocities are sharply defined. Therefore the electron and the proton would both move with the constant center of mass velocity $\boldsymbol{V}$ along straight lines. Motion with a fixed distance between the two particles seems hardly compatible with their electromagnetic attraction, but Bohmian mechanics explains this in terms of an additional quantum potential generated by the wave function,

$$V_\psi(\boldsymbol{x}) = -\frac{\hbar^2}{2m|\psi(\boldsymbol{x})|}\Delta|\psi(\boldsymbol{x})|,$$

i.e. the wave function would also induce an additional force field in Bohmian mechanics.

However, motion with fixed separation between the electron and the proton should imply observation of an electric dipole moment for individual hydrogen atoms, contrary to ordinary quantum mechanics.

On the other hand, motion of the electron and the proton right on top of each other is an appealing classical picture, but is incompatible with the positive nucleus plus negative electron hull structure of atoms that follows e.g. from the van der Waals equation of state for gases (which gives atomic radii between 1 and 2 Å) and Rutherford scattering (which tells us two things: only the positive charge is concentrated in the nucleus, and the nucleus has only a radius of a few femtometers).

To avoid this negative verdict, we might argue that we should rather consider a cold gas of Bohmian hydrogen atoms to understand the implications of the Bohmian interpretation for the ground state wave function.

In a cold gas of Bohmian hydrogen atoms the static distance between the electron and the proton would be distributed according to $|\langle\boldsymbol{x}_e - \boldsymbol{x}_p|1,0,0\rangle|^2$. There would be many hydrogen atoms with the electron sitting right on top of the proton, but there would also be a lot of hydrogen atoms with a large separation and a corresponding static electric dipole moment $\boldsymbol{d} = e(\boldsymbol{x}_p - \boldsymbol{x}_e)$. Standard quantum mechanics in Born's interpretation does not predict an electric dipole moment in any of the hydrogen atoms, because an electron would only appear to have a particular location if we specifically perform a measurement asking for the location. However, in Bohmian mechanics, the electron and proton would exist as particles at all times with fixed relative location, and therefore there should be an average dipole moment per atom in the ground state with magnitude $\langle|\boldsymbol{d}|\rangle = e\langle r\rangle = 3ea/2$.

These dipole moments might be randomly distributed and therefore we might not observe a macroscopic dipole moment. However, we could align these dipole moments with a weak static external electric field. The field strength would be much weaker than the internal field strength in hydrogen, to ensure that the ground state wave function is not perturbed. In addition to any induced electric dipole moment in the Bohmian hydrogen atoms (which would also exist in the same way for the standard quantum mechanical hydrogen atoms) there would be a macroscopic dipole moment from orientation polarization. This would be a real difference from the standard quantum mechanical cold hydrogen gas. Therefore I disagree with claims that Bohmian mechanics is just a different ontological interpretation of non-relativistic quantum mechanics. Trying to make pilot wave theories work is certainly tempting, but I cannot consider Bohmian mechanics as a serious competitor to standard quantum mechanics with the Born interpretation of quantum states.