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Radial Potentials and the Hydrogen Atom

18.1 Radial Potentials

If V is any radial function on $\mathbb{R}^3$, let $\hat{H} = -(\hbar^2/(2m))\Delta + V$ be the corresponding Hamiltonian operator, acting on $L^2(\mathbb{R}^3)$. We will look for solutions to the time-independent Schrödinger equation $\hat{H}\psi = E\psi$ of the form $\psi(\mathbf{x}) = p(\mathbf{x})f(|\mathbf{x}|)$, where f is a smooth function on $(0,\infty)$ and p is a harmonic polynomial on $\mathbb{R}^3$ that is homogeneous of degree l.

Proposition 18.1 *Let p be a harmonic polynomial on $\mathbb{R}^3$ that is homogeneous of degree l and let f be a smooth function on $(0,\infty)$. Let ψ be the function on $\mathbb{R}^3\backslash\{0\}$ given by*

$$\psi(\mathbf{x}) = p(\mathbf{x})f(|\mathbf{x}|). \tag{18.1}$$

Then on $\mathbb{R}^3\backslash\{0\}$ we have

$$\Delta\psi(\mathbf{x}) = p(\mathbf{x})\left[\frac{d^2f}{dr^2} + \frac{2(l+1)}{r}\frac{df}{dr}\right].$$

Proof. We begin with the case $l = 0$, so that p is a constant—which we take to be 1—and ψ is just the radial function $f(|\mathbf{x}|)$. Then

$$\begin{aligned}\frac{\partial}{\partial x_j}f(|\mathbf{x}|) &= \frac{df}{dr}\frac{d}{dx_j}\sqrt{x_1^2+x_2^2+x_3^2}\\ &= \frac{df}{dr}\frac{x_j}{|\mathbf{x}|}\end{aligned}$$

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and so

$$\sum_{j=1}^{3} \frac{\partial^2}{\partial x_j^2} f(|\mathbf{x}|) = \sum_{j=1}^{3} \left[\frac{d^2 f}{dr^2} \frac{x_j^2}{|\mathbf{x}|^2} + \frac{df}{dr} \left(\frac{1}{|\mathbf{x}|} - \frac{x_j^2}{|\mathbf{x}|^3} \right) \right]$$
$$= \frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr}.$$

For the general case, the product rule for the Laplacian gives

$$\Delta\psi = (\Delta p) f(|\mathbf{x}|) + 2\nabla p \cdot \nabla f(|\mathbf{x}|) + p\Delta f(|\mathbf{x}|).$$

Now, $\Delta p = 0$ by assumption. Furthermore, since $f(|\mathbf{x}|)$ is radial, its gradient points in the radial direction. Thus, only the radial component of ∇p is relevant. Moreover, on each ray through the origin, p behaves like a constant times r^l. Thus, the r-derivative of p is $(l/r)p$, giving

$$\Delta\psi = \frac{2l}{r} p \frac{df}{dr} + p \frac{d^2 f}{dr^2} + \frac{2}{r} p \frac{df}{dr},$$

which simplifies to the desired expression. ■

Although the decomposition of functions in Definition 17.18 is for many purposes the most convenient one, it is not quite the customary way of turning spherical harmonics into functions on $\mathbb{R}^3$. Conventionally, one works in polar coordinates and considers functions of the form

$$\psi(r, \theta, \phi) = p(\theta, \phi) g(r),$$

where p is the restriction to S^2 of an element of V_l. We can express this decomposition in rectangular coordinates as

$$\psi(\mathbf{x}) = p\left(\frac{\mathbf{x}}{|\mathbf{x}|} \right) g(|\mathbf{x}|) = \frac{p(\mathbf{x})}{|\mathbf{x}|^l} g(|\mathbf{x}|).$$

We can then obtain a more customary form of Proposition 18.1 as follows.

Proposition 18.2 *Suppose $p \in V_l$ and f is a smooth function on $(0, \infty)$, and let ψ by the function on $\mathbb{R}^3 \backslash \{0\}$ given by*

$$\psi(\mathbf{x}) = p\left(\frac{\mathbf{x}}{|\mathbf{x}|} \right) g(|\mathbf{x}|).$$

Then

$$(\Delta\psi)(r\mathbf{x}) = p(\mathbf{x}) \left[\frac{d^2 g}{dr^2} + \frac{2}{r} \frac{dg}{dr} - \frac{l(l+1)}{r^2} g(r) \right] \tag{18.2}$$

for all $\mathbf{x} \in S^2$ and $r \in (0, \infty)$.

Proof. Since p is homogeneous of degree l,

$$p\left(\frac{\mathbf{x}}{|\mathbf{x}|}\right) = \frac{p(\mathbf{x})}{|\mathbf{x}|^l}.$$

Thus,

$$\psi(\mathbf{x}) = p(\mathbf{x})\left(\frac{f(|\mathbf{x}|)}{|\mathbf{x}|^l}\right).$$

Applying Proposition 18.1 gives

$$\Delta\psi(\mathbf{x}) = p(\mathbf{x})\left[\frac{d^2}{dr^2} + \frac{2(l+1)}{r}\frac{d}{dr}\right]\left(\frac{f(r)}{r^l}\right).$$

From here it is straightforward but unilluminating calculation to verify the formula in the proposition. ■

Still another way to write functions on $\mathbb{R}^3$ is in the form

$$\psi(\mathbf{x}) = \frac{1}{|\mathbf{x}|}p\left(\frac{\mathbf{x}}{|\mathbf{x}|}\right)h(|\mathbf{x}|), \tag{18.3}$$

so that $h(r) = rg(r)$. If we replace $g(r)$ by $h(r)/r$ in (18.2), we obtain, after a short calculation,

$$(\Delta\psi)(r\mathbf{x}) = \frac{1}{|\mathbf{x}|}p(\mathbf{x})\left[\frac{d^2h}{dr^2} - \frac{l(l+1)}{r^2}h(r)\right], \quad \mathbf{x} \in S^2. \tag{18.4}$$

Writing wave functions in the form (18.3) is convenient because we then have, for any radial potential,

$$-\frac{\hbar^2}{2m}\Delta\psi + V(|\mathbf{x}|)\psi = \frac{1}{|\mathbf{x}|}p(\mathbf{x})\left[-\frac{\hbar^2}{2m}\frac{d^2h}{dr^2} + V_{\text{eff}}(r)h(r)\right], \tag{18.5}$$

where V_{eff} is the *effective potential* given by

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{18.6}$$

Note that the quantity in square brackets in (18.5) is just an ordinary one-dimensional Schrödinger operator, since the first derivative term in (18.2) has been eliminated. Despite the naturalness of the form (18.3), it is the form (18.1) that is ultimately most convenient for finding the bound states of the hydrogen atom Hamiltonian.

Now, as the discussion following Proposition 9.34 illustrates, even if ψ is square-integrable over $\mathbb{R}^3\backslash\{0\}$ and $\Delta\psi$ is square-integrable over $\mathbb{R}^3\backslash\{0\}$, ψ may not be in the domain of the Laplacian, since the distributional Laplacian of ψ may contain a term that is supported at the origin. In the case of the hydrogen atom, however, we will consider functions ψ of the form (18.1) where f and df/dr are bounded near the origin and have exponential decay near infinity. Proposition 9.35 then tells us that ψ is in the domain of Δ.

18.2 The Hydrogen Atom: Preliminaries

A hydrogen atom is formed out of a single electron that is "bound" to a proton by means of the electromagnetic attraction between the oppositely charged particles. The study of the hydrogen atom is a very important test case in quantum mechanics, and the ability of the Schrödinger equation to explain the observed energy levels of hydrogen was a crucial early success of the theory.

A proton is approximately 1,800 times as massive as an electron. Thus, to first approximation, we may think of the location of the proton as being fixed, with the electron "orbiting" around this location. A more careful analysis considers both the proton and the electron as orbiting around their center of mass. The Hamiltonian for the relative position of the two particles is precisely that of a particle orbiting around a fixed center, *except* that the mass of the electron is replaced by the reduced mass μ of the electron–proton system. (See Exercise 1.) Here, as in Proposition 2.16 in the classical case,

$$\mu = \frac{m_e m_p}{m_e + m_p},$$

where m_e and m_p are the masses of the proton and electron, respectively. Since $m_p \gg m_e$, the reduced mass is nearly the same as the mass of the electron.

After separating out the motion of the center of mass, we are left with the following Hamiltonian for the relative position of the electron:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta - \frac{Q^2}{|\mathbf{x}|}, \tag{18.7}$$

where Q is the charge of the electron. (We use a system of units, such as "electrostatic" or "Gaussian" units, in which the Coulomb constant is equal to 1.) It follows from Theorem 9.38 that $\hat{H}$ is self-adjoint on $\mathrm{Dom}(\Delta)$ and that $\hat{H}$ is bounded below.

Note that the classical Hamiltonian $H(\mathbf{x}, \mathbf{p})$ for a hydrogen atom is *not* bounded below. After all, we can simply take $\mathbf{p} = 0$ and take $\mathbf{x}$ very close to the origin. This unboundedness would cause strange behavior for a hypothetical classical hydrogen atom. After all, modeling a hydrogen atom using the $1/r$ potential is only an approximation. We are using an electrostatic formula for the force, the correct one when the positions of the particles are held fixed, in a dynamical situation. A more realistic model of hydrogen takes into account radiation, that is, the interaction of the charged electron with the electromagnetic fields. Classically, a negatively charge particle orbiting a positively charged nucleus would radiate, thus giving up energy to the electromagnetic fields. The classical particle would spiral rapidly toward the origin, with the particle's energy going to $-\infty$ and the energy of the electromagnetic field going to $+\infty$. Thus, if hydrogen were

made up of *classical* charged particles, the electron would go into a "death spiral" and emit a giant burst of electromagnetic radiation.

Fortunately for us, this is not how real particles behave! In actuality, the electron is a quantum particle. A quantum electron "orbiting" a proton can still give up energy to the electromagnetic field. The Hamiltonian for the *quantum* hydrogen atom, however, is bounded below, as a consequence of Theorem 9.38. Thus, the electron can only drop to its ground state (the state of lowest energy), at which point it becomes stable.

18.3 The Bound States of the Hydrogen Atom

Our goal in this section is to find the eigenvectors for the Hamiltonian $\hat{H}$ in (18.7) with negative eigenvalues. Such eigenvectors constitute "bound states," that is, states in which the electron is bound to the proton. For each negative number E, we look at the eigenspace V_E for $\hat{H}$ with eigenvalue E, that is, the space of all $\psi \in \mathrm{Dom}(\hat{H})$ satisfying $\hat{H}\psi = E\psi$. Since $\hat{H}$ is self-adjoint and, therefore, closed, this eigenspace will be a closed subspace of $L^2(\mathbb{R}^3)$. Since, also, $\hat{H}$ commutes with rotations, V_E will be invariant under the usual action (Definition 17.1) of $\mathsf{SO}(3)$ on $L^2(\mathbb{R}^3)$. Thus, by the discussion at the end of Sect. 17.7, V_E decomposes as a direct sum of *finite-dimensional*, irreducible $\mathsf{SO}(3)$-invariant subspaces.

We now look for such subspaces of V_E. In the following theorem, we assume that the radial part of the wave function (the function f in the notation $V_{l,f}$ in Definition 17.18) has a certain very special form. After analyzing this case, we argue that we have found in this way all of the eigenvectors for $\hat{H}$ with negative eigenvalues.

Theorem 18.3 *For each positive integer n, let*

$$E_n = -\frac{\mu Q^4}{2\hbar^2}\frac{1}{n^2} \tag{18.8}$$

where Q is the charge of the electron and μ is the reduced mass of the electron–proton system, and let

$$\rho_n(\mathbf{x}) = \frac{\sqrt{8\mu\,|E_n|}}{\hbar}\,|\mathbf{x}|\,.$$

Then for each $l = 0, 1, \ldots, n-1$, there exists a polynomial $L_{n,l}$ such that for each homogeneous harmonic polynomial q of degree l, the function

$$\psi(\mathbf{x}) = q(\mathbf{x})e^{-\rho_n(\mathbf{x})/2}L_{n,l}(\rho_n(\mathbf{x})) \tag{18.9}$$

satisfies

$$\hat{H}\psi = E_n\psi.$$

It follows from Proposition 9.35 that the functions ψ in (18.9) belong to $\mathrm{Dom}(\Delta)$ and thus, by Theorem 9.38, to $\mathrm{Dom}(\hat{H})$. The polynomials $L_{n,l}$ are the Laguerre polynomials. The coefficient of $-1/n^2$ in the formula (18.8) for E_n is the Rydberg constant (compare Sect. 1.2.1).

Let us see how to connect Theorem 18.3 to the usual expression for the hydrogen atom eigenvectors in the physics literature. In the first place, physicists choose a certain basis $q_{l,m}$ for the space of harmonic polynomials, which is—up to normalization constants—the basis in Theorem 17.4. In the second place, physicists write the solutions in spherical coordinates. When changing to spherical coordinates, we should keep in mind that $q_{l,m}$ is homogeneous of degree l and that $\rho_n(\mathbf{x})$ is just a constant multiple of the distance from the origin. We obtain, then, the following expression:

$$\psi_{n,l,m}(r,\theta,\phi) = Y_{l,m}(\theta,\phi)\rho_n^l e^{-\rho_n/2} L_{n,l}(\rho_n), \tag{18.10}$$

where $Y_{l,m}(\theta,\phi)$ is the restriction to the unit sphere of $p_{l,m}$.

Proof. If E is a negative real number, we look for solutions to $\hat{H}\psi = E\psi$ of the form $q(\mathbf{x})f(|\mathbf{x}|)$, where $q \in V_l$. Provided that $f(r)$ and $f'(r)$ are bounded near the origin, Proposition 9.35 allows us to compute $\Delta\psi$ on $\mathbb{R}^3\backslash\{0\}$ without worrying about whether ψ is differentiable at the origin. Using Proposition 18.1, the equation for f is

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2f}{dr^2} + \frac{2(l+1)}{r}\frac{df}{dr}\right] - \frac{Q^2}{r}f(r) = Ef(r). \tag{18.11}$$

For large r, where the two terms that involve a factor of $1/r$ become negligible, and so

$$-\frac{\hbar^2}{2\mu}\frac{d^2f}{dr^2} \approx Ef. \tag{18.12}$$

Recalling that E is negative, (18.12) tells us that near infinity, f should behave like a combination of a growing and a decaying exponential. Since we want square-integrable solutions, we require that only the exponentially decaying term be present.

We therefore postulate a solution of the form

$$f(r) = \exp\left\{-\frac{\sqrt{2\mu\,|E|}}{\hbar}r\right\} g(r), \tag{18.13}$$

for some function g. If we plug (18.13) into (18.11) for f, there are canceling terms equal to $Eg(r)$ on each side, leaving

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2g}{dr^2} - 2\frac{\sqrt{2\mu\,|E|}}{\hbar}\frac{dg}{dr} + \frac{2(l+1)}{r}\frac{dg}{dr} - \frac{2(l+1)}{r}\frac{\sqrt{2\mu\,|E|}}{\hbar}g(r)\right]$$
$$= \frac{Q^2}{r}g(r).$$

We now introduce the new variable $\rho = (\sqrt{8\mu\,|E|}/\hbar)r$. After making this change of variable, we find that each term in square brackets obtains a factor of $8\mu\,|E|\,/\hbar^2$, so that our equation becomes

$$-\frac{\hbar^2}{2\mu}\frac{8\mu\,|E|}{\hbar^2}\left[\frac{d^2g}{d\rho^2}-\frac{dg}{d\rho}+\frac{2(l+1)}{\rho}\frac{dg}{d\rho}-\frac{(l+1)}{\rho}g(\rho)\right]=\frac{2\sqrt{2\mu\,|E|}}{\hbar}\frac{Q^2}{\rho}g(\rho).$$

Multiplying through by ρ and simplifying yields the equation.

$$\rho\frac{d^2g}{d\rho^2}-\rho\frac{dg}{d\rho}+2(l+1)\frac{dg}{d\rho}+\left[\frac{Q^2\sqrt{\mu}}{\hbar\sqrt{2\,|E|}}-(l+1)\right]g(\rho)=0. \tag{18.14}$$

If we postulate for g a power series $\sum_{k=0}^{\infty}a_k\rho^k$, we obtain the following recurrence relations for the coefficients:

$$a_{k+1}=a_k\frac{[k+l+1-\lambda]}{k[(k+1)+2(l+1)]} \tag{18.15}$$

where

$$\lambda=\frac{Q^2\sqrt{\mu}}{\hbar\sqrt{2\,|E|}}.$$

The series for g will terminate, yielding a polynomial solution to (18.14), provided that λ is an integer n with $n \geq l+1$. We can then solve for the energy in terms of n as follows:

$$|E|=\frac{\mu Q^4}{2n^2\hbar^2}.$$

Recalling that E is negative, we have obtained the desired form for the energy levels. Furthermore, the condition $n \geq l+1$ is the same as $l \leq n-1$. Finally, if we plug in the formula for ρ in terms of r and the formula for f in terms of g, we obtain the form of the solution stated in the theorem. ∎

It is important to emphasize that the functions in Theorem 18.3 *do not* span the entire Hilbert space $L^2(\mathbb{R}^3)$. After all, these functions are all eigenvectors for $\hat{H}$ with *negative* eigenvalues. If these vectors spanned $L^2(\mathbb{R}^3)$, then the expectation value of the energy would always be negative. But it is easy to produce functions ψ in the domain of $\hat{H}$ for which $\langle\psi,\hat{H}\psi\rangle>0$. Simply take ψ to be a Gaussian wave packet with mean position far from the origin and with very large mean momentum. Then $\langle\psi,V\psi\rangle$ will be close to zero but $\langle\psi,P^2\psi\rangle$ will be large and positive. Nevertheless, it can be shown that the functions in Theorem 18.3 span the negative energy subspace of $L^2(\mathbb{R}^3)$. It is possible to analyze also the positive part of the spectrum of $\hat{H}$, but the spectrum above zero is purely continuous and represents a hydrogen atom that has ionized, that is, in which the electron has escaped from the proton.

Theorem 18.4 *As n varies over all positive integers, l varies from 0 to $n-1$, and g varies over all homogeneous harmonic polynomials of degree l, the eigenvectors in Theorem 18.3 span the negative-energy subspace of $L^2(\mathbb{R}^3)$, that is, the range of the projection $\mu^{\hat{H}}((-\infty, 0))$, where $\mu^{\hat{H}}$ is the projection-valued measure associated to $\hat{H}$ by the spectral theorem.*

Proof. The proof requires results from spectral theory that go beyond the machinery that we have developed in Chaps. 9 and 10, and which we cannot reproduce in full here. Specifically, we make use of Theorem V.5.7 of [27], which tells us that the negative-energy portion of the spectrum of $\hat{H}$ is discrete, consisting of eigenvalues of finite multiplicity accumulating only at zero.

We indicate briefly why the above result holds. If A and B are unbounded self-adjoint operators, let us say that B is a *relatively compact* perturbation of A if $A(B-\lambda I)^{-1}$ is a compact operator for every λ in the resolvent set of B. According to Lemma V.5.8 of [27], the potential energy operator for the hydrogen atom is a relatively compact perturbation of the kinetic energy operator. This is a strengthening of what we showed in the proof of Theorem 9.38, namely that the potential energy operator is relatively bounded with respect to the kinetic energy operator, with relative bound less than 1. The proof of relative compactness relies on the fact that the potential for the hydrogen atom goes to zero at infinity.

Meanwhile, let us say that λ belongs to the *essential spectrum* of an unbounded self-adjoint operator A if either λ is a nonisolated point in $\sigma(A)$ or λ is an eigenvalue for A with infinite multiplicity. According to Theorem IV.5.35 of [27], a relatively compact perturbation of a self-adjoint operator does not change the essential spectrum. Thus, the essential spectrum of $\hat{H}$ is equal to the essential spectrum of the kinetic energy operator, which is certainly contained in $[0, \infty)$, since the kinetic energy operator is non-negative. It follows that any point in the negative-energy part of the spectrum of $\hat{H}$ must be an isolated point in $\sigma(\hat{H})$ and an eigenvalue of finite multiplicity.

In light of the preceding result, there is no continuous spectrum for $\hat{H}$ below zero, and we need only look for *square-integrable* eigenvectors. Since, also, each eigenspace for $\hat{H}$ with eigenvalue $E < 0$ is finite dimensional, it will decompose as a direct sum of irreducible, $\mathsf{SO}(3)$-invariant subspaces. Such subspaces, according to Proposition 17.19, are always of the form $V_{l,f}$ for some l and f, where $V_{l,f}$ is as in Definition 17.18. Thus, we look for functions ψ of the form $\psi(\mathbf{x}) = p(\mathbf{x})f(|\mathbf{x}|)$ such that $\hat{H}\psi = E\psi$ for some $E < 0$.

Now, if a function of the form $p(\mathbf{x})f(|\mathbf{x}|)$ is to be an eigenfunction of the Hamiltonian, f must satisfy the differential equation (18.11). By elementary results from the theory of linear ordinary differential equations, this equation has precisely two linearly independent solutions, for any value of E. Both solutions can be constructed by postulating a solution of the

form (18.13), introducing the new variable ρ, and then using a power series expansion for $g(\rho)$ (Exercise 9). One of the solutions for $g(\rho)$ will have a power series starting with $\rho^{-(2l+1)}$, in which case $\psi(\mathbf{x})$ will blow up like $1/|\mathbf{x}|^{(l+1)}$ near the origin; such a function is not in the domain of the Hamiltonian (Exercise 14 in Chap. 9). The other solution for $g(\rho)$ will start with ρ^0 and may be obtained by using the form (18.13), changing from the variable r to the variable ρ, and then using the recurrence relation (18.15) to define the coefficients of a power series. If the resulting series does not terminate, it is not hard to see that the terms will behave for large k like the series for e^{ρ}. Since the function f is equal to $e^{-\rho/2}g(\rho)$, this function will grow like $e^{\rho/2}$ near infinity, which means that ψ will not be in $L^2(\mathbb{R}^3)$. Thus, to get a square-integrable solution, the series for $g(\rho)$ must terminate, in which case ψ is one of the functions in Theorem 18.3. ■

Corollary 18.5 *Each eigenvalue E_n, as given in Theorem 18.3, has multiplicity n^2.*

Proof. According to Theorem 18.4, the eigenvectors in Theorem 18.3 constitute all of the eigenvectors for $\hat{H}$ with eigenvalue E_n. The number of independent eigenvectors with eigenvalue E_n is thus the sum of the dimensions of the spaces V_l of spherical harmonics, with $l = 0, 1, \ldots, n-1$. This number is, by Theorem 17.12,

$$\sum_{l=0}^{n-1}(2l+1) = n^2,$$

as claimed. ■

18.4 The Runge–Lenz Vector in the Quantum Kepler Problem

In Sect. 2.6, we showed that the classical Kepler problem can be solved almost completely by making use of the Runge–Lenz vector, which is a conserved quantity. The quantum version of the Runge–Lenz vector commutes with the Hamiltonian and can elucidate a number of special properties of the quantum Kepler problem, which we typically think of as describing a hydrogen atom. In particular, the Runge–Lenz vector will help to explain (1) the simple form $-R/n^2$ of the negative energies of the hydrogen atom and (2) the apparent coincidence by which energy of the states in (18.9) is independent of l for a given n. Note that the rotational symmetry of the problem explains why the energy of the states in (18.9) is independent of the choice of the harmonic polynomial q. Nevertheless, rotational symmetry cannot explain why states for different values of l—and thus different radial dependence in the wave function—have the same energy. This

apparent coincidence will be explained by an additional symmetry of the problem, that is expressible in terms of the Runge–Lenz vector. See also Sect. 7 of [17] for a somewhat different (but related) explanation for the structure of the eigenvalues of the hydrogen atom and their multiplicities.

There are several computations involving the Runge–Lenz vector that, while elementary, are laborious. Those computations are deferred to Sect. 18.6.

18.4.1 Some Notation

To keep the notation as simple as possible, we will adopt in this section Einstein's *summation convention*, which states that repeated indices are always summed on, even if there is no summation sign written. In this section, the sum will always range from 1 to 3. Using this convention, we write, say, the dot product of two vectors $\mathbf{u}, \mathbf{v}$ in $\mathbb{R}^3$ as $\mathbf{u} \cdot \mathbf{v} = u_j v_j$,where the summation convention frees us from having to write out explicitly the sum over j.

We will make frequent use of the *totally antisymmetric symbol* ε_{jkl}, where j, k, and l range from 1 to 3, defined as follows,

Definition 18.6 *For $j, k, l \in \{1, 2, 3\}$, define ε_{jkl} by the formula*

$$\varepsilon_{jkl} = \begin{cases} 1 & \text{if } (j,k,l) \text{ is an even permutation of } (1,2,3) \\ -1 & \text{if } (j,k,l) \text{ is an odd permutation of } (1,2,3) \\ 0 & \text{if any two of } j,k,l \text{ are equal} \end{cases} .$$

Thus, for example, $\varepsilon_{321} = -1$ and $\varepsilon_{212} = 0$. The commutation relations for the basis $\{F_1, F_2, F_3\}$ for $\mathsf{so}(3)$ may be written (using the summation convention!) as

$$[F_j, F_k] = \varepsilon_{jkl} F_l. \tag{18.16}$$

For instance, if we take $j = 1$ and $k = 2$ in (18.16), then the sum on l gives a nonzero value only when $l = 3$, and we recover the relation $[F_1, F_2] = F_3$.

18.4.2 The Classical Runge–Lenz Vector, Revisited

We have already introduced, in Sect.2.6, the Runge–Lenz vector $\mathbf{A}$ in the classical mechanics of a particle moving in a $1/r$ potential. We require a few more properties of $\mathbf{A}$ before turning to the quantum version. We consider a classical particle in $\mathbb{R}^3$ with Hamiltonian given by

$$H(\mathbf{x}, \mathbf{p}) = \frac{|\mathbf{p}|^2}{2\mu} - \frac{Q^2}{|\mathbf{x}|}. \tag{18.17}$$

This is just the Hamiltonian for the classical Kepler problem, except that we replace the mass m of the planet by the reduced mass μ of the electron–proton system, and we replace the constant $k := mMG$ by Q^2.

For the Hamiltonian in (18.17), the Runge–Lenz vector is given by the formula

$$\mathbf{A}(\mathbf{x},\mathbf{p}) = \frac{1}{\mu Q^2}\mathbf{p}\times\mathbf{J} - \frac{\mathbf{x}}{|\mathbf{x}|},$$

where $\mathbf{J} := \mathbf{x}\times\mathbf{p}$ is the angular momentum. By Proposition 2.34, the Runge–Lenz vector is a conserved quantity for the classical Kepler problem, in addition to H and $\mathbf{J}$, which are conserved quantities for any radial potential. By results of Sect. 2.6, we have the following relations among these conserved quantities:

$$\begin{aligned}\mathbf{A}\cdot\mathbf{J} &= 0\\ |\mathbf{A}|^2 &= 1 + \frac{2H}{\mu Q^4}\,|\mathbf{J}|^2.\end{aligned}$$

Lemma 18.7 *The Runge–Lenz vector* $\mathbf{A}$ *and the Hamiltonian* H *in (18.17) satisfy the following Poisson bracket relations:*

$$\begin{aligned}\{A_j, H\} &= 0\\ \{A_j, A_m\} &= -\frac{2}{\mu Q^4}\varepsilon_{jml}J_l H.\end{aligned} \tag{18.18}$$

We have already shown that the Runge–Lenz vector is a conserved quantity (Proposition 2.34), which is equivalent (Proposition 2.25) to saying that the Poisson bracket of A_j with H is zero, as claimed. The proof of (18.18) is deferred to Sect. 18.6. We now introduce certain combinations of the Runge–Lenz vector, the angular momentum, and the Hamiltonian that form a Lie algebra under the Poisson bracket. In the construction of these functions, we need to take a square root of the Hamiltonian, which necessitates separating the positive-energy and negative-energy parts of the phase space. Our interest is primarily in the negative-energy case.

Definition 18.8 *Let* U^- *denote the negative-energy part of the classical phase space,*

$$U^- = \left\{ (\mathbf{x},\mathbf{p}) \in \mathbb{R}^6 \,\middle|\, H(\mathbf{x},\mathbf{p}) < 0 \right\}.$$

Consider on U^- *the normalized Runge–Lenz vector* $\mathbf{B}$ *given by*

$$\mathbf{B} = \sqrt{\frac{\mu Q^4}{2\,|H|}}\;\mathbf{A}.$$

Define also vector-valued functions $\mathbf{I}$ *and* $\mathbf{K}$ *on* U^- *by*

$$\mathbf{I} = \frac{\mathbf{J}+\mathbf{B}}{2}; \quad \mathbf{K} = \frac{\mathbf{J}-\mathbf{B}}{2}.$$

Theorem 18.9 *The functions* $\mathbf{I}$ *and* $\mathbf{K}$ *Poisson-commute with the Hamiltonian and satisfy the following Poisson-bracket relations on the negative-energy set* U^-*:*

$$\begin{aligned}\{I_j, I_k\} &= \varepsilon_{jkl} I_l \\ \{K_j, K_k\} &= \varepsilon_{jkl} K_l \\ \{I_j, K_k\} &= 0.\end{aligned}$$

The functions $\mathbf{I}$ *and* $\mathbf{K}$ *also satisfy the following algebraic relations:*

$$|\mathbf{I}|^2 = |\mathbf{K}|^2 = \frac{\mu Q^4}{8\,|H|}.$$

In Theorem 18.9, we use the summation convention introduced in the previous subsection. The proof of this theorem is elementary but rather laborious, and is deferred to Sect. 18.6.

The span of the functions I_1, I_2, I_3 and K_1, K_2, K_3 on U^-, which is the same as the span of the functions B_1, B_2, B_3 and J_1, J_2, J_3, forms a 6-dimensional Lie algebra under the Poisson bracket. Comparing the Poisson-bracket relations among the I's and among the K's to the relations among the basis elements F_1, F_2, F_3 for $\mathsf{so}(3)$, we see that the span of the I's and the span of the K's are both isomorphic to $\mathsf{so}(3)$ [or, if you prefer, to $\mathsf{su}(2)$]. Since also each I_j commutes with each K_k, the 6-dimensional Lie algebra spanned by the I's and the K's is isomorphic to $\mathsf{so}(3) \oplus \mathsf{so}(3)$. Meanwhile, as demonstrated in Exercise 4, $\mathsf{so}(3) \oplus \mathsf{so}(3)$ is isomorphic to the Lie algebra $\mathsf{so}(4)$. Since all the I's and K's Poisson-commute with the Hamiltonian, we say that the Kepler problem has $\mathsf{so}(4)$ symmetry. This is in contrast to the dynamics of a particle moving in $\mathbb{R}^3$ in the force generated by a typical radial potential, which has only $\mathsf{so}(3)$ symmetry.

To be more precise, "$\mathsf{so}(4)$ symmetry" prevails only on the negative-energy subset U^- of the classical phase space. On the positive-energy subset U^+, the span of the functions B_1, B_2, B_3 and J_1, J_2, J_3 again forms a 6-dimensional Lie algebra. This Lie algebra, however, is *not* isomorphic to $\mathsf{so}(4)$, but rather to $\mathsf{so}(3,1)$, where $\mathsf{so}(3,1)$ is the Lie algebra of the group of 4×4 matrices that preserve the quadratic form $x_1^2+x_2^2+x_3^2-x_4^2$. The reason the formulas on U^+ are different from those on U^- is that calculations of the relevant Poisson brackets involves the function $H/|H|$, which has the value 1 on U^+ and the value -1 on U^-. (The factor of H comes from Lemma 18.7 and the factor of $|H|$ from the factor of $\sqrt{|H|}$ in the definition of $\mathbf{B}$.)

18.4.3 The Quantum Runge–Lenz Vector

We now introduce the quantum counterpart $\hat{\mathbf{A}}$ of the classical Runge–Lenz vector $\mathbf{A}$. The quantum Runge–Lenz satisfies most of the same properties as the classical version, with a few small but crucial "quantum corrections."

Definition 18.10 *Define the* ***quantum Runge–Lenz vector*** *by*

$$\hat{\mathbf{A}} = \frac{1}{\mu Q^2}\frac{1}{2}\left(\mathbf{P}\times\hat{\mathbf{J}} - \hat{\mathbf{J}}\times\mathbf{P}\right) - \frac{\mathbf{X}}{|\mathbf{X}|}.$$

Note that in the quantum case, $-\hat{\mathbf{J}}\times\mathbf{P}$ is not the same as $\mathbf{P}\times\hat{\mathbf{J}}$, because of the noncommutativity of the factors. The particular combination of $\mathbf{P}\times\hat{\mathbf{J}}$ and $\hat{\mathbf{J}}\times\mathbf{P}$ in Definition 18.10 is used because it is yields a self-adjoint operator. The Runge–Lenz vector can also be computed as

$$\hat{\mathbf{A}} = \frac{1}{\mu Q^2}\left(\mathbf{P}\times\hat{\mathbf{J}} - i\hbar\mathbf{P}\right) - \frac{\mathbf{X}}{|\mathbf{X}|}, \tag{18.19}$$

as will be verified in Sect. 18.6.

In the interests of keeping the exposition manageable, we will not concern ourselves in what follows with determining the precise domains on which various identities hold.

Proposition 18.11 *The quantum Runge–Lenz vector* $\hat{\mathbf{A}}$ *satisfies the following relations:*

$$\begin{aligned}\hat{\mathbf{A}}\cdot\hat{\mathbf{J}} &= \hat{\mathbf{J}}\cdot\hat{\mathbf{A}} = 0\\ \hat{\mathbf{A}}\cdot\hat{\mathbf{A}} &= 1 + \frac{2\hat{H}}{\mu Q^4}\left(\hat{\mathbf{J}}\cdot\hat{\mathbf{J}} + \hbar^2\right).\end{aligned} \tag{18.20}$$

Note that there is a "quantum correction" in (18.20); the factor of $\mathbf{J}\cdot\mathbf{J}$ in the classical expression for $\mathbf{A}\cdot\mathbf{A}$ is replaced by $\hat{\mathbf{J}}\cdot\hat{\mathbf{J}}+\hbar^2$. This correction gives rise to a quantum correction in (18.22), which in turn is essential to getting the correct value for the energy eigenvalues in Corollary 18.17. The proof of this result and the other results of this section are deferred to Sect. 18.6.

Lemma 18.12 *The quantum Runge–Lenz vector* $\hat{\mathbf{A}}$ *and the Hamiltonian* $\hat{H}$ *satisfy the following commutation relations:*

$$\begin{aligned}\frac{1}{i\hbar}[\hat{A}_j,\hat{H}] &= 0\\ \frac{1}{i\hbar}[\hat{A}_j,\hat{A}_m] &= -\frac{2}{\mu Q^4}\varepsilon_{jml}\hat{J}_l\hat{H}.\end{aligned} \tag{18.21}$$

Note that since $\hat{H}$ commutes with rotations, it commutes with the angular momentum operators $\hat{J}_l$. Thus, in (18.21), we could just as well write $\hat{H}\hat{J}_l$ in place of $\hat{J}_l\hat{H}$. As in the classical case, if we normalize the components of the Runge–Lenz vector by dividing by the square root of the Hamiltonian, then these operators together with the angular momentum operators form a 6-dimensional Lie algebra.

Definition 18.13 *Let V^- denote the negative-energy subspace of $L^2(\mathbb{R}^3)$, that is, the range of the spectral projection $\mu^{\hat{H}}((-\infty, 0))$. Let $|\hat{H}|$ denote the restriction to V^- of the operator $-\hat{H}$. On V^-, define operators $\hat{\mathbf{B}}$ by*

$$\hat{\mathbf{B}} = \frac{\mu Q^2}{\sqrt{2\mu|\hat{H}|}}\,\hat{\mathbf{A}}.$$

Define also operators $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$, as in the classical case, by

$$\hat{\mathbf{I}} = \frac{\hat{\mathbf{J}} + \hat{\mathbf{B}}}{2}; \quad \hat{\mathbf{K}} = \frac{\hat{\mathbf{J}} - \hat{\mathbf{B}}}{2}.$$

It is possible to define the absolute value of any self-adjoint operator by means of the functional calculus. However, since the restriction of $\hat{H}$ to V^- is, by definition, negative definite, the restriction of $|\hat{H}|$ to V^- coincides with the restriction to V^- of $-\hat{H}$. The operator $1/\sqrt{|\hat{H}|}$ is the operator with a restriction to the energy eigenspace with eigenvalue E_n that is $1/\sqrt{|E_n|}I$. The components of $\hat{\mathbf{B}}$ are unbounded operators, defined on suitable dense subspaces of the Hilbert space V^-.

Theorem 18.14 *The operators $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ commute with the Hamiltonian $\hat{H}$ and satisfy the following commutation relations:*

$$\begin{aligned}
\frac{1}{i\hbar}[\hat{I}_j, \hat{I}_k] &= \varepsilon_{jkl}\hat{I}_l \\
\frac{1}{i\hbar}[\hat{K}_j, \hat{K}_k] &= \varepsilon_{jkl}\hat{K}_l \\
\frac{1}{i\hbar}[\hat{I}_j, \hat{K}_k] &= 0.
\end{aligned}$$

These operators also satisfy the following algebraic relations:

$$\hat{\mathbf{I}} \cdot \hat{\mathbf{I}} = \hat{\mathbf{K}} \cdot \hat{\mathbf{K}} = \frac{\mu Q^4}{8|\hat{H}|} - \frac{\hbar^2}{4}. \tag{18.22}$$

18.4.4 Representations of $\mathsf{so}(4)$

In light of the commutation relations in Theorem 18.14, we can define a representation π of the Lie algebra $\mathsf{so}(4) \cong \mathsf{so}(3) \oplus \mathsf{so}(3)$ on the negative-energy subspace V^- as follows:

$$\pi(F_j, 0) = \frac{1}{i\hbar}\hat{I}_j; \quad \pi(0, F_j) = \frac{1}{i\hbar}\hat{K}_j. \tag{18.23}$$

It is therefore desirable to classify the irreducible finite-dimensional representations of $\mathsf{so}(3) \oplus \mathsf{so}(3)$, which we do in the following proposition.

Proposition 18.15 *Suppose V_k and V_l are irreducible representations of* $\mathsf{so}(3)$ *of dimensions* $2k+1$ *and* $2l+1$*, respectively. Then $V_k \otimes V_l$ is irreducible when viewed as a representation of* $\mathsf{so}(3) \oplus \mathsf{so}(3)$ *as in Remark 16.49. Furthermore, every irreducible finite-dimensional representation of* $\mathsf{so}(3) \oplus \mathsf{so}(3)$ *is isomorphic to $V_k \otimes V_l$ for a unique ordered pair (k, l).*

For any representation $V_k \otimes V_l$ of $\mathsf{so}(3) \oplus \mathsf{so}(3)$*, define Casimir operators C_1 and C_2 by the formula*

$$C_1 = \sum_{j=1}^{3} \pi_k(F_j)^2 \otimes I; \quad C_2 = \sum_{j=1}^{3} I \otimes \pi_l(F_j)^2.$$

Then we have

$$C_1 = -k(k+1)I; \quad C_2 = -l(l+1)I.$$

Proof. To classify the irreducible representations of $\mathsf{so}(3) \oplus \mathsf{so}(3)$, we could appeal to the general theory of representations of direct sums of Lie algebras. It is not hard, however, to give a direct proof using the same sort of reasoning we used in the classifications of irreducible representations of $\mathsf{so}(3)$. We will omit the details of this computation. The result on the Casimir operators follows easily from Proposition 17.8. ∎

In any finite-dimensional subspace of V^- that is invariant and irreducible under the action of $\mathsf{so}(3) \oplus \mathsf{so}(3)$ in (18.23), the Casimir operators are given by $C_1 = -\hat{\mathbf{I}} \cdot \hat{\mathbf{I}}/\hbar^2$ and $C_2 = -\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}/\hbar^2$. Since, by Theorem 18.14, $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}} = \hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$ on V^-, all of the irreducible representations of $\mathsf{so}(3) \oplus \mathsf{so}(3)$ that arise inside V^- will be of the form $V_k \otimes V_k$.

Theorem 18.16 *Let $W^{(n)}$ denote the eigenspace for the Hamiltonian with eigenvalue E_n. Then $W^{(n)}$ is invariant and irreducible under the action of* $\mathsf{so}(3) \oplus \mathsf{so}(3)$ *in (18.23). More specifically, we have the isomorphism*

$$W^{(n)} \cong V_k \otimes V_k,$$

as representations of $\mathsf{so}(3) \oplus \mathsf{so}(3)$*, where $k = (n-1)/2$ and where V_k is the irreducible representation of* $\mathsf{so}(3)$ *of dimension $2k+1 = n$.*

Corollary 18.17 *If n, k, and $W^{(n)}$ are as in Theorem 18.16, then for all $\psi \in W^{(n)}$, we have*

$$\hat{\mathbf{I}} \cdot \hat{\mathbf{I}} \psi = \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \psi = \hbar^2 k(k+1).$$

Using (18.22), the eigenvalue E_n of $\hat{H}$ on $W^{(n)}$ can be solved for as

$$E_n = -\frac{\mu Q^4}{8\hbar^2 \left(k + \frac{1}{2}\right)^2} = -\frac{\mu Q^2}{2\hbar^2 n^2}.$$

The expression for E_n in Corollary 18.17 is the same as in Theorem 18.3. The remarkable thing about the proof of Theorem 18.17 is that it is purely

algebraic, relying only on the commutation relations among the operators $\hat{I}_k$ and $\hat{K}_l$, along with the relationship (18.22) between the Hamiltonian operator $\hat{H}$ and the $\hat{I}_k$'s and $\hat{K}_l$'s.

Proof of Corollary 18.17. It is easily seen that the operators $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}}$ and $\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$, when restricted to an irreducible subspace for the action of $\mathsf{so}(3) \oplus \mathsf{so}(3)$, are equal to $-\hbar^2 C_1$ and $-\hbar^2 C_2$, where C_1 and C_2 are the Casimir operators appearing in Proposition 18.15. Thus, if $W^{(n)}$ is isomorphic to $V_k \otimes V_k$, with $k = (n-1)/2$, then $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}}$ and $\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$ will be equal to $\hbar^2 k(k+1)I$, as claimed. On the other hand, $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}}$ and $\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$ are related to the Hamiltonian $\hat{H}$ by (18.22), from which we can solve for E_n. ∎

Proof of Theorem 18.16. Since each component of $\mathbf{A}$ and $\hat{\mathbf{J}}$ commutes with $\hat{H}$, each component of $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ will also commute with $\hat{H}$. Each eigenspace of $\hat{H}$ is therefore invariant under the action of $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$. Since the $\hat{I}$'s and $\hat{K}$'s are self-adjoint and $W^{(n)}$ is finite dimensional, $W^{(n)}$ will decompose as a direct sum of irreducible invariant subspaces. By Proposition 18.15, these irreducible subspaces will be of the form $V_k \otimes V_l$, where V_k and V_l are irreducible representations of $\mathsf{so}(3)$ of dimension $2k+1$ and $2l+1$, respectively. But now, the operators $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}}$ and $\hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$, when restricted to one of the irreducible subspaces of $W^{(n)}$, are equal to $-\hbar^2 C_1$ and $-\hbar^2 C_2$, where C_1 and C_2 are the Casimir operators appearing in Proposition 18.15. Since $\hat{\mathbf{I}} \cdot \hat{\mathbf{I}} = \hat{\mathbf{K}} \cdot \hat{\mathbf{K}}$ on all of V^-, the eigenvalues of C_1 and C_2 must be equal on each irreducible subspace of $W^{(n)}$. Thus, we must have $k = l$, meaning that only irreducible subspaces of the form $V_k \otimes V_k$ arise.

Now, under the isomorphism of some irreducible subspace of $W^{(n)}$ with $V_k \otimes V_k$, the operators $\hat{I}_k$ and $\hat{K}_k$ act as $i\hbar F_k \otimes I$ and $i\hbar I \otimes F_k$, respectively, where the F_k's are the usual basis for $\mathsf{so}(3)$. Since $\hat{\mathbf{J}} = \hat{\mathbf{I}} + \hat{\mathbf{K}}$, each $\hat{J}_k$ acts as $i\hbar(F_k \otimes I + I \otimes F_k)$. This means that $V_k \otimes V_k$, under the action of the $\hat{J}_k$'s, can be thought of as a tensor product of two representations of $\mathsf{so}(3)$, viewed as another representation of $\mathsf{so}(3)$ as in Definition 16.48. Viewed this way, $V_k \otimes V_k$ decomposes as in Proposition 17.23 as

$$V_k \otimes V_k \cong V_0 \oplus V_1 \oplus \cdots \oplus V_{2k}. \tag{18.24}$$

On the other hand, we know from Theorem 18.3 that $W^{(n)}$ decomposes under the action of $\mathsf{so}(3)$ as

$$V_0 \oplus V_1 \oplus \cdots \oplus V_{n-1}. \tag{18.25}$$

Thus, the space of the form $V_k \otimes V_k$ must be all of $W^{(n)}$; if there were another term then the trivial representation V_0 would occur more than once in $W^{(n)}$. This being the case, matching the decompositions (18.24) and (18.25) requires that $2k = n-1$, as claimed in the theorem. ∎

The proof of Theorem 18.16 relies to some extent on the results of Sect. 18.3. Using only algebraic manipulations involving the Runge–Lenz vector, however, we could still argue that the eigenvalues of $\hat{H}$ must be of the form given in Corollary 18.17. We would not, however, know that for

every positive integer n, the number E_n is actually an eigenvalue for $\hat{H}$. We would also not know that each eigenspace $W^{(n)}$ is irreducible under the action of $\mathsf{so}(4)$; conceivably, based only on the algebra, $W^{(n)}$ could have, say, dimension $2n^2$ instead of n^2.

18.5 The Role of Spin

The spin of the electron is 1/2. As discussed in Sect. 17.8, this means that the Hilbert space for an electron is $L^2(\mathbb{R}^3)\hat{\otimes}V_{1/2}$, where $V_{1/2}$ is a 2-dimensional vector space that carries an irreducible projective unitary representation of $\mathsf{SO}(3)$. Up to now, we have neglected the spin in our calculations. The reason for this omission is simple: to first approximation, the spin plays no role in the calculation. Specifically, in the simplest model of a hydrogen atom with spin, the Hamiltonian is simply $\hat{H} \otimes I$, where $\hat{H}$ is the operator in (18.7), acting on $L^2(\mathbb{R}^3)$. For any $n > 0$, we can obtain a basis of eigenvectors for $\hat{H} \otimes I$ with eigenvalue E_n by taking vectors of the form $\psi_{n,l,m} \otimes e_j$, where the $\psi_{n,l,m}$'s are as in (18.10) and where $\{e_1, e_2\}$ forms a basis for $V_{1/2}$.

Now, from the point of view of rotational symmetry, the basis $\psi_{n,l,m} \otimes e_j$ is not the most natural one. Rather, we should decompose the eigenspaces into irreducible invariant subspaces for the (projective) action of $\mathsf{SO}(3)$, where $\mathsf{SO}(3)$ acts on *both* $L^2(\mathbb{R}^3)$ and $V_{1/2}$. We have already decomposed the eigenspaces inside $L^2(\mathbb{R}^3)$ into irreducible invariant subspaces, namely the span of $\psi_{n,l,m}$ where n and l are fixed and m varies. Thus, to obtain the irreducible invariant subspaces inside $L^2(\mathbb{R}^3)\hat{\otimes}V_{1/2}$, we use the method of "addition of angular momentum" from Sect. 17.9. According to Proposition 17.22, $V_l \otimes V_{1/2}$ is irreducible if $l = 0$ and isomorphic to $V_{l+1/2} \oplus V_{l-1/2}$ if $l > 0$. Consider, for example, the case $n = 3$, $l = 1$, the so-called "3p states" in traditional chemistry terminology. Since $V_1 \otimes V_{1/2}$ decomposes as $V_{3/2} \oplus V_{1/2}$, when we take spin into account, we obtain a 4-dimensional space and a 2-dimensional space. We can obtain bases for these spaces by tracing through the proof of Proposition 17.22.

The decomposition described in the previous paragraph is essential when considering the "fine structure" of hydrogen. Our model of hydrogen using the Hamiltonian (18.7) is only a first approximation. More realistic models take into account various corrections, including radiative corrections, a finite size for the nucleus, and "spin–orbit coupling," among other things. The notion of spin–orbit coupling adds a term into the Hamiltonian involving the operator $\hat{\mathbf{J}} \cdot \sigma$, where σ_1, σ_2, and σ_3 are the operators describing the action of $\mathsf{so}(3)$ on $V_{1/2}$. When this term is included, the Hamiltonian is no longer of the form $A \otimes I$ for some operator A on $L^2(\mathbb{R}^3)$. Thus, we can no longer simply append the spin to the end of the computation, but must take it into account from the beginning.

The various corrections to the Hamiltonian for the hydrogen atom have the effect of reducing the multiplicities of the eigenvalues. Almost any correction we make, for example, will destroy the independence of the eigenvalue on l for a given n, simply because the correction terms in the Hamiltonian will not commute with the quantum Runge–Lenz vector. Nevertheless, all of the corrections that make up the fine structure of hydrogen preserve the rotational symmetry of the problem. Thus, the same irreducible representations of $\mathsf{SO}(3)$ that we had in the simple model will appear after the corrections are made. For $n = 2$, $l = 1$, for example, we will still have a 4-dimensional space and 2-dimensional space, but these two spaces will no longer have the same energy.

18.6 Runge–Lenz Calculations

In this section, we fill in many of the computations that we passed over without proof in Sect. 18.4. Although all the calculations are, in principle, elementary, there are a number of nonobvious tricks that help simplify the algebra. We will make frequent use of the concepts of functions that transform like vectors (on the classical side) and of vector operators (on the quantum side), including Propositions 17.25 and 17.27 (Sect. 17.10). In particular, we note that the position $\mathbf{x}$, the momentum $\mathbf{p}$, the angular momentum $\mathbf{j}$, and the Runge–Lenz vector $\mathbf{A}$ all transform like vectors, and that the corresponding quantum quantities are all vector operators. (Compare Exercise 7.) In the "ε" notation of Sect. 18.4.1, Proposition 17.27 takes the form

$$\frac{1}{i\hbar}[C_j, \hat{J}_k] = \frac{1}{i\hbar}[\hat{J}_j, C_k] = \varepsilon_{jkl} C_l. \tag{18.26}$$

In the quantum mechanical calculations, there are a number of "quantum corrections," in which dot products and cross products of vector operators do not behave as they do in the classical case.

Lemma 18.18 *The ε-function in Definition 18.6 satisfies the relations*

$$\varepsilon_{jkl}\varepsilon_{jmn} = \delta_{km}\delta_{ln} - \delta_{kn}\delta_{lm}$$
$$\varepsilon_{jkl}\varepsilon_{jkm} = 2\delta_{lm}.$$

The proof of these results is not difficult and is left to the reader (Exercise 6). The following identities involving the cross product of vector operators will be useful to us.

Lemma 18.19 *If* $\mathbf{C}$, $\mathbf{D}$, *and* $\mathbf{E}$ *are arbitrary vector operators, we have*

$$\mathbf{C} \cdot (\mathbf{D} \times \mathbf{E}) = (\mathbf{C} \times \mathbf{D}) \cdot \mathbf{E} \tag{18.27}$$
$$\mathbf{C} \times \mathbf{D} + \mathbf{D} \times \mathbf{C} = \varepsilon_{jkl}[C_k, D_l] \tag{18.28}$$
$$\mathbf{C} \times \mathbf{C} = \frac{1}{2}\varepsilon_{jkl}[C_k, C_l]. \tag{18.29}$$

In particular, if the different components of $\mathbf{C}$ *commute, then* $\mathbf{C} \times \mathbf{C} = 0$. *Finally,*

$$(\mathbf{C} \times (\mathbf{D} \times \mathbf{E}))_j = C_k D_j E_k - C_k D_k E_j. \tag{18.30}$$

As special cases of these results, we have

$$\hat{\mathbf{J}} \times \mathbf{P} + \mathbf{P} \times \hat{\mathbf{J}} = 2i\hbar \mathbf{P} \tag{18.31}$$

$$\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}} \tag{18.32}$$

Note that if the entries of $\mathbf{D}$ and $\mathbf{E}$ commute, then the right-hand side of (18.30) reduces to the classical expression, $(\mathbf{C} \cdot \mathbf{E})\mathbf{D} - (\mathbf{C} \cdot \mathbf{D})\mathbf{E}$. Using (18.31), we can easily verify the alternative expression (18.19) for the Runge–Lenz vector.

Proof. The right-hand side of (18.27) is computed as $\varepsilon_{jkl} C_k D_l E_j$. If we note that $\varepsilon_{jkl} = \varepsilon_{klj}$ and then relabel the indices, we obtain $\varepsilon_{jkl} C_j D_k E_l$, which is equal to the left-hand side of (18.27). For (18.28), we compute that

$$\begin{aligned} (\mathbf{C} \times \mathbf{D} + \mathbf{D} \times \mathbf{C})_j &= \varepsilon_{jkl} C_k D_l + \varepsilon_{jkl} D_k C_l \\ &= \varepsilon_{jkl} C_k D_l + \varepsilon_{jkl} C_l D_k - \varepsilon_{jkl} [C_l, D_k]. \end{aligned} \tag{18.33}$$

If we note that $\varepsilon_{jkl} = -\varepsilon_{jlk}$ and then relabel the indices k and l, we see that $\varepsilon_{jkl} C_l D_k = -\varepsilon_{jkl} C_k D_l$, so that the first two terms in the second line of (18.33) cancel. The remaining term can be put into the claimed form by relabeling the indices k and l. The identity (18.29) is just the $\mathbf{D} = \mathbf{C}$ case of (18.28). Finally, (18.30) follows easily from Lemma 18.18.

To obtain (18.31) and (18.32), we apply (18.28) and (18.29), respectively. Since both $\hat{\mathbf{J}}$ and $\mathbf{P}$ are vector operators, the desired result follows easily from Lemma 18.18. ■

We now turn to the proofs of the results of Sect. 18.4. We prove only the quantum versions of the results, since the classical results are extremely similar, except that certain quantum corrections can be ignored.

Proof of Lemma 18.12, First Part. We begin by showing that $\hat{A}_j$ commutes with $\hat{H}$ for each j. Since $\hat{H}$ commutes with $\hat{\mathbf{J}}$, we have

$$[\hat{A}_j, \hat{H}] = \frac{1}{\mu Q^2} \frac{1}{2} \left(\varepsilon_{jkl} [P_k, \hat{H}] \hat{J}_l - \hat{J}_k [P_l, \hat{H}] \right) - \left[\frac{X_j}{|\mathbf{X}|}, \hat{H} \right].$$

Meanwhile, since the P's commute among themselves, we have

$$[P_k, \hat{H}] = -Q^2 \left[P_k, \frac{1}{|\mathbf{X}|} \right] = -i\hbar Q^2 \frac{X_k}{|\mathbf{X}|^3}.$$

Thus,

$$\begin{aligned}\varepsilon_{jkl}[P_k,\hat{H}]\hat{J}_l &= -i\hbar Q^2\varepsilon_{jkl}\varepsilon_{lmn}\frac{X_k}{|\mathbf{X}|^3}X_mP_n\\ &= -i\hbar Q^2(\delta_{jm}\delta_{kn}-\delta_{jn}\delta_{km})\frac{X_k}{|\mathbf{X}|^3}X_mP_n\\ &= -i\hbar Q^2\frac{1}{|\mathbf{X}|^3}(X_nX_jP_n-X_mX_mP_j)\\ &= -i\hbar Q^2\frac{1}{|\mathbf{X}|^3}\left(X_j(\mathbf{X}\cdot\mathbf{P})-(\mathbf{X}\cdot\mathbf{X})P_j\right). \qquad (18.34)\end{aligned}$$

We compute $\varepsilon_{jkl}\hat{J}_k[P_l,\hat{H}]$ in a similar way. Note that $\hat{J}_k=\varepsilon_{kmn}X_mP_n=\varepsilon_{kmn}P_nX_m$, since X_m and P_n commute except when $m=n$, in which case $\varepsilon_{kmn}=0$. The result is

$$\varepsilon_{jkl}\hat{J}_k[P_l,\hat{H}]=-i\hbar(P_j(\mathbf{X}\cdot\mathbf{X})-(\mathbf{P}\cdot\mathbf{X})X_j)\frac{1}{|\mathbf{X}|^3}.$$

Meanwhile, since the X's commute among themselves, we have

$$\begin{aligned}&\left[\frac{X_j}{|\mathbf{X}|},\hat{H}\right]\\ &=\left[\frac{X_j}{|\mathbf{X}|},\frac{P^2}{2\mu}\right]\\ &=\frac{1}{2\mu}\left[\frac{X_j}{|\mathbf{X}|},P_k\right]P_k+\frac{1}{2\mu}P_k\left[\frac{X_j}{|\mathbf{X}|},P_k\right]\\ &=\frac{i\hbar}{2\mu}\left(\frac{1}{|\mathbf{X}|}\delta_{jk}-\frac{X_jX_k}{|\mathbf{X}|^3}\right)P_k+\frac{i\hbar}{2\mu}P_k\left(\frac{1}{|\mathbf{X}|}\delta_{jk}-\frac{X_jX_k}{|\mathbf{X}|^3}\right)\\ &=\frac{i\hbar}{2\mu}\left(\frac{1}{|\mathbf{X}|}P_j-\frac{X_j}{|\mathbf{X}|^3}(\mathbf{X}\cdot\mathbf{P})\right)+\frac{i\hbar}{2\mu}\left(P_j\frac{1}{|\mathbf{X}|}-(\mathbf{P}\cdot\mathbf{X})\frac{X_j}{|\mathbf{X}|^3}\right). \qquad (18.35)\end{aligned}$$

It is now a simple matter to compute $[\hat{A}_j,\hat{H}]$ by combining (18.34) and (18.35) and verify that everything cancels. We have, for example, a term involving $(X_j/|\mathbf{X}|^3)(\mathbf{X}\cdot\mathbf{P})$ in (18.34) and a canceling term in (18.35). ■

Before proceeding with the remaining results concerning the Runge–Lenz vector, we verify some results that will be needed later. There are some quantum corrections compared to the corresponding classical results.

Lemma 18.20 *As in the classical case, the following "orthogonality" relations among vector operators hold:*

$$\hat{\mathbf{J}}\cdot\mathbf{P}=\mathbf{P}\cdot\hat{\mathbf{J}}=0 \qquad (18.36)$$

$$\hat{\mathbf{J}}\cdot\mathbf{X}=\mathbf{X}\cdot\hat{\mathbf{J}}=0 \qquad (18.37)$$

$$(\mathbf{P}\times\hat{\mathbf{J}})\cdot\hat{\mathbf{J}}=\hat{\mathbf{J}}\cdot(\mathbf{P}\times\hat{\mathbf{J}})=0. \qquad (18.38)$$

Meanwhile, there is a quantum correction in the dot product between $\mathbf{P}$ *and* $\mathbf{P} \times \hat{\mathbf{J}}$, *as follows:*

$$\mathbf{P} \cdot (\mathbf{P} \times \hat{\mathbf{J}}) = 0 \tag{18.39}$$

$$(\mathbf{P} \times \hat{\mathbf{J}}) \cdot \mathbf{P} = 2i\hbar(\mathbf{P} \cdot \mathbf{P}). \tag{18.40}$$

Finally, we have

$$(\mathbf{P} \times \hat{\mathbf{J}}) \cdot (\mathbf{P} \times \hat{\mathbf{J}}) = (\mathbf{P} \cdot \mathbf{P})(\hat{\mathbf{J}} \cdot \hat{\mathbf{J}}) \tag{18.41}$$

$$\mathbf{X} \cdot (\mathbf{P} \times \hat{\mathbf{J}}) = \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \tag{18.42}$$

$$(\mathbf{P} \times \hat{\mathbf{J}}) \cdot \mathbf{X} = \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} + 2i\hbar \mathbf{P} \cdot \mathbf{X}. \tag{18.43}$$

Proof. By (18.27) and (18.29), we have

$$\hat{\mathbf{J}} \cdot \mathbf{P} = (\mathbf{X} \times \mathbf{P}) \cdot \mathbf{P} = \mathbf{X} \cdot (\mathbf{P} \times \mathbf{P}) = 0,$$

since the different components of $\mathbf{P}$ commute. The same reasoning shows that $\mathbf{P} \cdot \hat{\mathbf{J}}$, $\hat{\mathbf{J}} \cdot \mathbf{X}$, and $\mathbf{X} \cdot \hat{\mathbf{J}}$ are all zero. To compute $(\mathbf{P} \times \hat{\mathbf{J}}) \cdot \hat{\mathbf{J}}$, we first use (18.27), then use (18.32), and then use that $\mathbf{P} \cdot \hat{\mathbf{J}} = 0$. For $\hat{\mathbf{J}} \cdot (\mathbf{P} \times \hat{\mathbf{J}})$, we rewrite $\mathbf{P} \times \hat{\mathbf{J}}$ in terms of $\hat{\mathbf{J}} \times \mathbf{P}$, using (18.31). The correction term involves $\mathbf{P}$, which has a dot product of zero with $\hat{\mathbf{J}}$, and so the answer is again zero.

We use (18.27) and (18.29) again to establish (18.39). To get (18.40), we first rewrite $\mathbf{P} \times \hat{\mathbf{J}}$ in terms of $\hat{\mathbf{J}} \times \mathbf{P}$ using (18.31) and then apply (18.39). To establish (18.41), we apply (18.27) and then (18.30), giving

$$(\mathbf{P} \times \hat{\mathbf{J}}) \cdot (\mathbf{P} \times \hat{\mathbf{J}}) = P_j \hat{J}_k P_j \hat{J}_k - P_j J_k P_k \hat{J}_j. \tag{18.44}$$

The second term on the right-hand side of (18.44) is zero because $\hat{\mathbf{J}} \cdot \mathbf{P} = 0$. For the first term, we move $\hat{J}_k$ to the right past P_j. This generates the term we want plus a correction term equal to $i\hbar\varepsilon_{kjl} P_j P_l \hat{J}_k$. The correction term is zero because P_j and P_l commute and ε_{kjl} is changes sign under interchange of j and l. The identity (18.42) follows immediately from (18.27) and the definition of $\hat{\mathbf{J}}$. The identity (18.43) follows from (18.27) and (18.28). ∎

Lemma 18.21 *For all* j *and* m, *we have*

$$[(\mathbf{P} \times \hat{\mathbf{J}})_j, (\mathbf{P} \times \hat{\mathbf{J}})_m] = -i\hbar(\mathbf{P} \cdot \mathbf{P})\varepsilon_{jml} \hat{J}_l.$$

Proof. In computing $[P_k \hat{J}_l, P_n \hat{J}_o]$, we use repeatedly the product rule for commutators (Point 3 of Proposition 3.15). We obtain four terms, one of which is zero (the term involving $[P_k, P_n]$). We use Proposition 17.27 (in the form (18.26)) to evaluate all remaining terms, giving

$$\begin{aligned} &\frac{1}{i\hbar}[\varepsilon_{jkl} P_k \hat{J}_l, \varepsilon_{mno} P_n \hat{J}_o] \\ &= \varepsilon_{jkl}\varepsilon_{mno} \left(P_k [\hat{J}_l, P_n] \hat{J}_o + P_n P_k [\hat{J}_l, \hat{J}_o] + P_n [P_k, \hat{J}_o] \hat{J}_l \right). \end{aligned} \tag{18.45}$$

Let us compute the first of the three terms on the right-hand side of (18.45). Using Lemma 18.18 and the fact that $\mathbf{P}$ is a vector operator, we get

$$\begin{aligned}\varepsilon_{jkl}\varepsilon_{mno}P_k[\hat{J}_l, P_n]\hat{J}_o &= \varepsilon_{jkl}(\delta_{op}\delta_{ml} - \delta_{ol}\delta_{mp})P_kP_p\hat{J}_o \\ &= \varepsilon_{jkm}P_kP_p\hat{J}_p - \varepsilon_{jko}P_kP_m\hat{J}_o \\ &= \varepsilon_{jkm}P_k(\mathbf{P}\cdot\hat{\mathbf{J}}) - P_m(\mathbf{P}\times\hat{\mathbf{J}})_j.\end{aligned}$$

If we compute the second and third terms similarly, we obtain

$$\begin{aligned}&\frac{1}{i\hbar}[\varepsilon_{jkl}P_k\hat{J}_l, \varepsilon_{mno}P_n\hat{J}_o] = \varepsilon_{jkm}P_k(\mathbf{P}\cdot\hat{\mathbf{J}}) - P_m(\mathbf{P}\times\hat{\mathbf{J}})_j \\ &+ (\mathbf{P}\times\mathbf{P})_j\hat{J}_m - \varepsilon_{jkm}P_k(\mathbf{P}\cdot\hat{\mathbf{J}}) + P_m(\mathbf{P}\times\hat{\mathbf{J}})_j - (\mathbf{P}\cdot\mathbf{P})\varepsilon_{jml}\hat{J}_l.\end{aligned}$$

Three of the above terms are zero (those involving $\mathbf{P}\cdot\hat{\mathbf{J}}$ or $\mathbf{P}\times\mathbf{P}$) and two other terms cancel, leaving us with

$$\frac{1}{i\hbar}[\varepsilon_{jkl}P_k\hat{J}_l, \varepsilon_{mno}P_n\hat{J}_o] = -(\mathbf{P}\cdot\mathbf{P})\varepsilon_{jml}\hat{J}_l,$$

as claimed. ■

We now continue with the proof of the properties of the Runge–Lenz vector.

Proof Proposition 18.11. From the first set of orthogonality relations in Lemma 18.20, we can see easily that $\hat{\mathbf{J}}\cdot\hat{\mathbf{A}} = \hat{\mathbf{A}}\cdot\hat{\mathbf{J}} = 0$. Meanwhile, using the expression (18.19) for $\hat{\mathbf{A}}$ and expanding out $\hat{\mathbf{A}}\cdot\hat{\mathbf{A}}$ yields, after a little simplification,

$$\begin{aligned}\hat{\mathbf{A}}\cdot\hat{\mathbf{A}} = 1 &+ \frac{1}{\mu^2Q^4}(\mathbf{P}\cdot\mathbf{P})\left(\hat{\mathbf{J}}\cdot\hat{\mathbf{J}} + \hbar^2\right) \\ &- \frac{1}{\mu Q^2}\left(2\hat{\mathbf{J}}\cdot\hat{\mathbf{J}}\frac{1}{|\mathbf{X}|} + i\hbar\left(\mathbf{P}\cdot\frac{\mathbf{X}}{|\mathbf{X}|} - \frac{\mathbf{X}}{|\mathbf{X}|}\cdot\mathbf{P}\right)\right).\end{aligned}$$

Now,

$$\frac{\mathbf{X}}{|\mathbf{X}|}\cdot\mathbf{P} - \mathbf{P}\cdot\frac{\mathbf{X}}{|\mathbf{X}|} = i\hbar\left(\frac{\delta_{kk}}{|\mathbf{X}|} - \frac{X_k}{|\mathbf{X}|^2}\frac{X_k}{|\mathbf{X}|}\right) = 2i\hbar\frac{1}{|\mathbf{X}|}.$$

Thus,

$$\hat{\mathbf{A}}\cdot\hat{\mathbf{A}} = 1 + \left((\hat{\mathbf{J}}\cdot\hat{\mathbf{J}}) + \hbar^2\right)\frac{2}{\mu Q^4}\left(\frac{(\mathbf{P}\cdot\mathbf{P})}{2\mu} - Q^2\frac{1}{|\mathbf{X}|}\right),$$

as claimed. ■

Proof of Lemma 18.12, Second Part. We write $\hat{\mathbf{A}}$ in the form given in (18.19). In computing the commutator of $\hat{A}_j$ with $\hat{A}_m$, we get several different types of terms, which we compute one at a time. Of course, the commutator of $X_j/|\mathbf{X}|$ with $X_m/|\mathbf{X}|$ is zero. The commutator of the $\mathbf{P}\times\hat{\mathbf{J}}$ terms has been computed in Lemma 18.21.

Meanwhile, to compute the commutator of $P_k\hat{J}_l$ with $X_m(1/|\mathbf{X}|)$, we again get four terms and, again, one of these is zero, namely the one involving $\{\hat{J}_l, 1/|\mathbf{X}|\}$, since $1/|\mathbf{X}|$ is invariant under rotations. We have, then,

$$\begin{aligned}
&\frac{1}{i\hbar}\left[\varepsilon_{jkl}P_k\hat{J}_l, X_m\frac{1}{|\mathbf{X}|}\right] \\
&= \varepsilon_{jkl}[P_k, X_m]\hat{J}_l\frac{1}{|\mathbf{X}|} + \varepsilon_{jkl}P_k[\hat{J}_l, X_m]\frac{1}{|\mathbf{X}|} + \varepsilon_{jkl}X_m\left[P_k, \frac{1}{|\mathbf{X}|}\right]\hat{J}_l \\
&= -\varepsilon_{jkl}\delta_{km}\hat{J}_l\frac{1}{|\mathbf{X}|} + \varepsilon_{jkl}\varepsilon_{lmn}P_kX_n\frac{1}{|\mathbf{X}|} + \varepsilon_{jkl}X_m\frac{X_k}{|\mathbf{X}|^3}\varepsilon_{lno}X_nP_o.
\end{aligned}$$

If we apply Lemma 18.18 and carry out some computations similar to ones we have already performed, we obtain

$$\begin{aligned}
\frac{1}{i\hbar}\left[\varepsilon_{jkl}P_k\hat{J}_l, X_m\frac{1}{|\mathbf{X}|}\right] &= -\varepsilon_{jml}\hat{J}_l\frac{1}{|\mathbf{X}|} + \delta_{jm}(\mathbf{P}\cdot\mathbf{X})\frac{1}{|\mathbf{X}|} \\
&+ X_mX_j\frac{1}{|\mathbf{X}|^3}(\mathbf{X}\cdot\mathbf{P}) - \left(P_m\frac{X_j}{|\mathbf{X}|} + \frac{X_m}{|\mathbf{X}|}P_j\right). \qquad (18.46)
\end{aligned}$$

In a commutator of the form $[\alpha_j + \beta_j, \alpha_m + \beta_m]$, the terms involving the commutator of an α with a β will be $[\alpha_j, \beta_m] + [\beta_j, \alpha_m]$, which is equal to $[\alpha_j, \beta_m] - [\alpha_m, \beta_j]$. This quantity is skew-symmetric j with m, meaning that it changes sign when we interchange j with m. Thus, terms in (18.46) that are symmetric in j and m will disappear when we compute the full commutator of $\hat{A}_j$ with $\hat{A}_m$. Thus, the second and third terms in (18.46) can be ignored. In the last term, we can commute P_m past X_j to obtain

$$P_m\frac{X_j}{|\mathbf{X}|} + \frac{X_m}{|\mathbf{X}|}P_j = \frac{X_j}{|\mathbf{X}|}P_m + \frac{X_m}{|\mathbf{X}|}P_j - i\hbar\left(\frac{\delta_{jm}}{|\mathbf{X}|} - \frac{X_jX_m}{|\mathbf{X}|^3}\right), \qquad (18.47)$$

which is also symmetric. Thus, only the first term in (18.46) contributes to the computation of $[\hat{A}_j, \hat{A}_m]$. This term is skew-symmetric in j and m and will be doubled when we compute $[\hat{A}_j, \hat{A}_m]$.

Now, it is straightforward to compute $[\varepsilon_{jkl}P_k\hat{J}_l, P_m]$ and $[P_j, X_m/|\mathbf{X}|]$ and to verify that these commutators are symmetric in j and m (Exercise 8) and therefore do not contribute to the computation of $[\hat{A}_j, \hat{A}_m]$. We are left, then, with the following

$$\begin{aligned}
\frac{1}{i\hbar}[\hat{A}_j, \hat{A}_m] &= -\frac{1}{\mu^2Q^4}\varepsilon_{jml}(\mathbf{P}\cdot\mathbf{P})\hat{J}_l + \frac{1}{\mu Q^2}2\varepsilon_{jml}\hat{J}_l\frac{1}{|\mathbf{X}|} \\
&= -\frac{2}{\mu Q^4}\varepsilon_{jml}\hat{J}_l\left(\frac{\mathbf{P}\cdot\mathbf{P}}{2\mu} - \frac{Q^2}{|\mathbf{X}|}\right),
\end{aligned}$$

which is what is claimed in the lemma. ■

Proof of Theorem 18.14. Since the Hamiltonian $\hat{H}$ is invariant under rotations, $\hat{H}$ commutes with each component of the angular momentum. We have also established that $\hat{H}$ commutes with each component of the Runge–Lenz vector. From this it follows easily that $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$ commute with the Hamiltonian.

Since A_k commutes with $\hat{H}$, it also commutes with any function of $\hat{H}$. It then follows from Lemma 18.12 that

$$\frac{1}{i\hbar}[\hat{B}_k, \hat{B}_l] = \frac{\mu Q^4}{2|\hat{H}|}[\hat{A}_k, \hat{A}_l] = -\frac{\mu Q^4}{2|\hat{H}|}\,\frac{2}{\mu Q^4}\varepsilon_{jml}\hat{J}_l\hat{H}.$$

Since $\hat{H}/|\hat{H}| = -I$ on the negative-energy subspace V^-, the above expression reduces to $\varepsilon_{jml}\hat{J}_l$. (The result on the positive-energy subspace will differ by a crucial minus sign from what we have on V^-.)

Meanwhile, since both $\hat{\mathbf{B}}$ and $\hat{\mathbf{J}}$ are vector operators, we have, by Proposition 17.27, $(1/(i\hbar))[\hat{B}_j, \hat{J}_k] = \varepsilon_{jkl}\hat{B}_l$ and $(1/(i\hbar))[\hat{J}_j, \hat{J}_k] = \varepsilon_{jkl}\hat{J}_l$. From the commutation relations among the $\hat{B}_j$'s and $\hat{J}_j$'s, it is an easy calculation to verify the claimed commutation relations among the components of $\hat{\mathbf{I}}$ and $\hat{\mathbf{K}}$. ∎

18.7 Exercises

1. Consider the quantum Hamiltonian for two particles in $\mathbb{R}^3$ interacting by means of a $1/r$ potential:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 - \frac{Q^2}{|\mathbf{x}^1 - \mathbf{x}^2|}.$$

Here, as in Sect. 3.11, Δ_1 is the Laplacian with respect to the variable $\mathbf{x}^1$ and Δ_2 is the Laplacian with respect to the variable $\mathbf{x}^2$. As in Sect. 2.3.3, introduce new variables consisting of the center of mass, $\mathbf{c} = (m_1\mathbf{x}^1 + m_2\mathbf{x}^2)/(m_1 + m_2)$, and the relative position, $\mathbf{y} = \mathbf{x}^1 - \mathbf{x}^2$.

Show that $\hat{H}_2$ can be expressed in these variables as

$$-\frac{\hbar^2}{2(m_1 + m_2)}\Delta_{\mathbf{c}} - \frac{\hbar^2}{2\mu}\Delta_{\mathbf{y}} - \frac{Q^2}{|\mathbf{y}|},$$

where μ is the reduced mass, given by $\mu = m_1m_2/(m_1 + m_2)$.

Note: In the new variables, $\hat{H}$ is the sum of two terms, one of which involves only the variable $\mathbf{c}$ and one of which involves only the variable $\mathbf{y}$. The term involving only $\mathbf{c}$ is the Hamiltonian for a free particle with mass $m_1 + m_2$, whereas the term involving only $\mathbf{y}$ is the Hamiltonian for a particle of mass μ moving in a $1/r$ potential.

2. Let $H(\mathbf{x},\mathbf{p}) = |\mathbf{p}|^2/(2\mu) - Q^2/|\mathbf{x}|$ denote the Hamiltonian for the classical Kepler problem in $\mathbb{R}^3$. Show that for every $\varepsilon > 0$, the region in $\mathbb{R}^6$ given by $\{(\mathbf{x},\mathbf{p}) \,|H(\mathbf{x},\mathbf{p}) < -\varepsilon\}$ has finite volume.

3. Let $\mathbb{H}$ denote the real span of the following four elements of $M_2(\mathbb{C})$:

$$\mathbf{1} := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \mathbf{i} := \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix};$$
$$\mathbf{j} := \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}; \quad \mathbf{j} := \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}.$$

   (a) Show that $\mathbb{H}$ forms an associative algebra over $\mathbb{R}$, under the operation of matrix multiplication, and that the following relations are satisfied:

$$\mathbf{i}^2 = \mathbf{j}^2 = \mathbf{k}^2 = -\mathbf{1}$$
$$\mathbf{ij} = -\mathbf{ji} = \mathbf{k}$$
$$\mathbf{jk} = -\mathbf{kj} = \mathbf{i}$$
$$\mathbf{ki} = -\mathbf{ik} = \mathbf{j}.$$

   The algebra $\mathbb{H}$ is (one particular realization of) the *quaternion algebra*.

   (b) Show that each nonzero element of $\mathbb{H}$ has a multiplicative inverse.

   Hint: Imitate the argument that each nonzero complex number has a multiplicative inverse.

4. Let $\mathbb{H}$ denote the quaternion algebra defined in Exercise 3. This exercise establishes explicitly an isomorphism between the Lie algebras $\mathsf{so}(4)$ and $\mathsf{so}(3) \oplus \mathsf{so}(3)$ (compare Definition 16.14).

   (a) Let V be the subspace of $\mathbb{H}$ spanned by $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$. Show that V forms a Lie algebra under the bracket $[\alpha,\beta] = \alpha\beta - \beta\alpha$ and that V is isomorphic as a Lie algebra to $\mathsf{so}(3)$.

   (b) Let $\mathrm{End}(\mathbb{H})$ denote the algebra of real-linear maps of $\mathbb{H}$ to itself. Given $\alpha \in V$, let $L_\alpha \in \mathrm{End}(\mathbb{H})$ be the "left multiplication by α" map, $L_\alpha(\beta) = \alpha\beta$, and let $R_\alpha \in \mathrm{End}(\mathbb{H})$ be the "right multiplication by α" map, $R_\alpha(\beta) = \beta\alpha$. Show that the maps $\alpha \mapsto L_\alpha$ and $\alpha \mapsto -R_\alpha$ are Lie algebra homomorphisms of V into $\mathrm{End}(\mathbb{H})$.

   (c) Consider the inner product on $\mathbb{H}$ in which $\{\mathbf{1},\mathbf{i},\mathbf{j},\mathbf{k}\}$ forms an orthonormal basis. Given $\alpha \in V$, show that

$$\langle L_\alpha\beta,\gamma\rangle = -\langle \beta, L_\alpha\gamma\rangle$$
$$\langle R_\alpha\beta,\gamma\rangle = -\langle \beta, R_\alpha\gamma\rangle\,.$$

That is to say, L_α and R_α belong to $\mathsf{so}(4)$, which we identify with the space of elements of $\mathrm{End}(\mathbb{H})$ that are skew-symmetric with respect to the inner product in Part (c).

(d) Show that the map $(\alpha, \beta) \mapsto L_\alpha - R_\beta$ is a Lie algebra isomorphism of $\mathsf{so}(3) \oplus \mathsf{so}(3)$ to $\mathsf{so}(4)$.

(e) Let D denote the diagonal subalgebra of $\mathsf{so}(3) \oplus \mathsf{so}(3)$, that is, the set of elements of the form (X, X). Show that the image of D under the isomorphism in Part (d) is the set of elements Y of $\mathsf{so}(4) \subset \mathrm{End}(\mathbb{H})$ having the following form with respect to the basis in Part (c):

$$Y = \begin{pmatrix} 0 & 0 \\ 0 & Z \end{pmatrix},$$

where $Z \in \mathsf{so}(3)$.

5. Describe explicitly the two subalgebras of $\mathsf{so}(4)$ corresponding to the two copies of $\mathsf{so}(3)$ in the isomorphism

$$\mathsf{so}(4) \cong \mathsf{so}(3) \oplus \mathsf{so}(3)$$

in Exercise 4.

6. Verify Lemma 18.18.

Hint: First show that $\varepsilon_{jkl}\varepsilon_{jmn} = 0$ unless $(k, l) = (m, n)$ or $(k, l) = (n, m)$.

7. In this exercise, we use the summation convention of Sect. 18.4.1.

(a) Show that for any 3×3 matrix M and any indices $j, k, l \in \{1, 2, 3\}$, we have

$$\varepsilon_{mno} M_{jm} M_{kn} M_{lo} = \varepsilon_{jkl} (\det M).$$

(b) Show that if $\mathbf{C}$ is a vector operator, then for all $R \in \mathsf{SO}(3)$, we have

$$\Pi(R) C_k \Pi(R)^{-1} = R_{lk} C_l.$$

(c) Show that the cross product of two vector operators is a vector operator.

Hint: Write the definition of a vector operator in the equivalent form

$$\mathbf{v} \cdot \mathbf{C} = \Pi(R)((R^{-1}\mathbf{v}) \cdot \mathbf{C})\Pi(R)^{-1}.$$

8. Compute $[\varepsilon_{jkl} P_k \hat{J}_l, P_m]$ and $[P_j, X_m / |\mathbf{X}|]$ and show that both of these quantities are symmetric in j and m, meaning that the value is unchanged if we interchange j and m.

9. Show that the Eq. (18.14) has two power series solutions for $g(\rho)$, one starting with $\rho^{-(2l+1)}$ and one starting with ρ^0.