Week 6 Worksheet Solutions
Fine Structure

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Exercise 1. Broken Symmetries. In classical mechanics, $\frac{1}{r}$ potentials have an additional conserved quantity that is rarely covered in introductory courses. This quantity is called the **Runge-Lenz vector**, and it is given by

$$\mathbf{F} = \frac{1}{m}\mathbf{p} \times \mathbf{L} - \frac{\gamma}{r}\mathbf{r},$$

where γ is the constant associated to the potential $V(r) = -\gamma/r$, e.g. $\gamma = e/4\pi\varepsilon_0$ or $\gamma = MG$.

a) If we replace all the classical dynamical variables in the above expression by quantum operators, explain why the result is ambiguous.
Hints: When we upgrade $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ to a quantum operator, note that $\mathbf{L} = -\mathbf{p} \times \mathbf{r}$ as operators. Why? Does $\mathbf{p} \times \mathbf{L} = -\mathbf{L} \times \mathbf{p}$ as operators?

b) It turns out[1] that the correct quantum mechanical version of $\mathbf{F}$ is

$$\mathbf{F} = \frac{1}{2m}\left(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}\right) - \frac{\gamma}{r}\mathbf{r}.$$

It can be shown in a lengthy computation that $[H, \mathbf{F}] = \mathbf{0}$, where H is the hydrogen atom hamiltonian (please try this at home), so $\mathbf{F}$ is a symmetry of the hydrogen atom. In fact, $\mathbf{F}$ is responsible for the "accidental" degeneracy in ℓ. Show that $[\mathbf{F}, \mathbf{L} \cdot \mathbf{S}]$ is not zero, so that fine structure breaks this symmetry (note(!) that $[\mathbf{L} \cdot \mathbf{S}, L^2] = 0$). This explains why the degeneracy in ℓ disappears once we consider fine structure effects.

c) Show that $[\mathbf{F}, p^4] \neq \mathbf{0}$ either, so this explains why the relativistic correction lifts the degeneracy in ℓ.

a) This is because $\mathbf{p} \times \mathbf{L} \neq -\mathbf{L} \times \mathbf{p}$, so it is unclear how to upgrade $\mathbf{p} \times \mathbf{L}$ to a quantum operator such that it behaves in the quantum mechanical world as the symmetry we expect classically (e.g. obeys

[1] The way you would prove this is by matching Poisson bracket relations with $\mathbf{F}$ in classical mechanics to corresponding ones in quantum mechanics (upgrading the Poisson brackets to commutators). This would then allow you to determine the right combination of $\mathbf{p} \times \mathbf{L}$ and $\mathbf{L} \times \mathbf{p}$ to take.

quantum analogous of Poisson bracket relations in classical mechanics). To see this, write the cross product in index notation:

$$(\mathbf{p} \times \mathbf{L})_k = \varepsilon_{ijk} p_i L_k = \varepsilon_{ijk} p_i \varepsilon_{klm} r_l p_m.$$

Since the commutator

$$[p_i, r_l] = -i\hbar\delta_{il},$$

we see that the above expression is not the same as

$$\varepsilon_{ijk}\varepsilon_{klm} r_l p_m p_i.$$

Indeed, in the sum we will at some point end up with terms where $l = i$.

b) **First Solution:** We can try to analyze the first term of $\mathbf{F}$. Note that we need only analyze either the $\mathbf{p} \times \mathbf{L}$ terms or the potential term, since commutators of r_i and p_j can only add factors of $i\hbar$. Since these will never be factors of m/γ or γ/m, the commutators of $\mathbf{L} \cdot \mathbf{S}$ with the first terms will never cancel those with the last term. Let's go ahead with this. First, note that if we write (using the triple product identity)

$$\mathbf{p} \times \mathbf{L} = \mathbf{r}\, p^2 - \mathbf{p}(\mathbf{r} \cdot \mathbf{p}),$$

the actual expansion of quantum operators will differ from this by some integer number of factors of $i\hbar\mathbf{p}$. Indeed, you can calculate that

$$\begin{aligned} [r_i, p^2] &= 2i\hbar p_i \\ \mathbf{r} \cdot \mathbf{p} &= 3i\hbar - \mathbf{p} \cdot \mathbf{r} \\ \mathbf{p}(\mathbf{r} \cdot \mathbf{p}) &= -i\hbar\mathbf{p} + (\mathbf{r} \cdot \mathbf{p})\mathbf{p}. \end{aligned}$$

Now, let's consider the commutator of $\mathbf{L} \cdot \mathbf{S}$ with the first term, $\mathbf{r}\, p^2$ above. Note that $\mathbf{S}$ commutes with all the operators in this term, so we can ignore it. Thus, we can calculate $[\mathbf{L}, \mathbf{r}\, p^2]$. Now, note that p^2 commutes with $\mathbf{L}$. This is because the hamiltonian commutes with $\mathbf{L}$, and the kinetic term in the hamiltonian is proportional to p^2. Thus, we need to compute

$$[\mathbf{L}, \mathbf{r}\, p^2] = [\mathbf{L}, \mathbf{r}]p^2.$$

So we only need to compute the commutator $[L_i, r_j]$. This will give us

$$[L_i, r_j] = \varepsilon_{lmi}[r_l p_m, r_j] = \varepsilon_{lmi} r_l [p_m, r_j] = -i\hbar\varepsilon_{lji} r_l.$$

So the total commutator is

$$[L_i, r_j\, p^2] = i\hbar\varepsilon_{ijk} r_k p^2.$$

Now, notice that by the same calculation as above,

$$[L_i, p_j] = \varepsilon_{kji} i\hbar p_k.$$

On the other hand, the commutator with the second term will always have separate components of $p_i p_j$ with $i \neq j$ by construction, so its commutator can't cancel the first term's commutator. This is a complex way to solve the problem, but it nonetheless is a solution. Let's investigate a simpler way.

Second Solution: As in the first solution, we can reduce to computing the commutator with either the potential term or the cross product terms. Let's try to compute the commutator with the potential term, which is proportional to $\mathbf{r}/r$. Its components are then r_i/r. As before, we need to consider

$$[L_i, r_j/r] = \varepsilon_{ikl} r_k [p_l, r_j/r],$$

where we again use the fact that r_k commutes with any function of r. Now, we use the fact that

$$[p_l, f(r)] = -i\hbar \partial_l f(r),$$

where ∂_l denotes the derivative of $f(r)$ with respect to r_l. The proof of this is simple:

$$[p_l, f(r)]\psi(r) = -i\hbar(\partial_l(f\psi) - f\,\partial_l\psi) = -i\hbar(\partial_l f)\psi.$$

But now we're done:

$$[L_i, r_j/r] = \varepsilon_{ikl} r_k \partial_l (r_j/r) = \varepsilon_{ikl} r_k \left(\frac{\delta_{jl}}{r} - \frac{r_j r_l}{r^2}\right) = \varepsilon_{ikj}\frac{r_k}{r}$$

which is nonzero. Since this term comes with a factor γ, this will only equal the contribution from the first term if m is chosen perfectly so as to cancel the constants appearing on γ. Thus, generically (i.e. for *any* value of m besides this special one), we have solved the problem.

c) It's enough to show that the commutator is nonzero again only for either the first terms or the last term. We have to use the last term in this case. If we tried to use the first terms, we would actually find that p^4 commutes with them! So let's compute

$$[p^4, r_i/r] = p^2[p^2, r_i/r] + [p^2, r_i/r]p^2,$$

so we only need to compute

$$[p^2, r_i/r] = p_j[p_j, r_i/r] + [p_j, r_i/r]p_j,$$

which is nonzero by the above calculation in the second solution for part b.