Problems #10 -- Solutions

QM1) a) The hydrogen wavefunction has a radial part and an angular part. Rewriting both the orbital angular momentum and the spin angular momentum as kets, the six possible product states come from all possible combinations of l=1 orbital states \((m = -1, 0 , +1)\) with \(s=1/2\) spin states \((m_s = -1/2, +1/2)\)...

\[
\begin{align*}
R_2 \begin{pmatrix} 1, -1 \end{pmatrix} | 1/2, 1/2 > \\
R_2 \begin{pmatrix} 1, 0 \end{pmatrix} | 1/2, 1/2 > \\
R_2 \begin{pmatrix} 1, +1 \end{pmatrix} | 1/2, 1/2 > \\
R_2 \begin{pmatrix} 1, -1 \end{pmatrix} | 1/2, -1/2 > \\
R_2 \begin{pmatrix} 1, 0 \end{pmatrix} | 1/2, -1/2 > \\
R_2 \begin{pmatrix} 1, +1 \end{pmatrix} | 1/2, -1/2 >
\end{align*}
\]

All of these generically are \(R_2 \begin{pmatrix} 1, m \end{pmatrix} | 1/2, m_s >\) or \(| R_{21} > | 1, m > | 1/2, m_s >\) in ket notation.

b) Both of the hydrogen parts are defined to be separately normalizable...

\[
\psi_{\text{hydrogen}} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)
\]

\[
\int (|\psi|)^2 dV = \int_0^\infty R_{n\ell}(r)^2 r^2 dr \int_0^{2\pi} d\theta \int_0^\pi (|Y_{\ell m}(\theta, \phi)|)^2 \sin(\theta) d\theta d\phi = 1
\]

since both \(\int_0^\infty R_{n\ell}(r)^2 r^2 dr = 1\) and \(\int_0^{2\pi} \int_0^\pi (|Y_{\ell m}(\theta, \phi)|)^2 \sin(\theta) d\theta d\phi = 1\)

The last angular normalization relation helps us understand the normalization \(< 1, m | 1, m > = 1\). The spin has its own separately normalized relation, \(< 1/2, m_s | 1/2, m_s > = 1\) without any alternative context, being an intrinsic spin. The radial ket inner product must then correspond to

\[
< R_{21} | R_{21} > = 1 = \int_0^\infty R_2(r)^2 r^2 dr
\]

This will help us with the meaning of the radial part of any expectation.

c) The "good" wavefunctions are the eigenstates of total angular momentum, which we discussed previously in the course. They are simultaneous eigenstates of \(J^2, J_z, L^2\) and \(S^2\) and are found from direct construction or by the table of Clebsch-Gordon coefficients, and have either \(j=3/2\) or \(j=1/2\) character, with eigenvalues \(\hbar^2 \cdot \frac{j(j+1)}{2}, \hbar \cdot m_j, \hbar^2 \cdot l(l+1)\) and \(\hbar^2 \cdot \frac{1}{2} \left( \frac{1}{2} + 1 \right)\) respectively.
Here they are:

\[ j = \frac{3}{2} \]

\[ | 3/2, 3/2 \rangle = | 1, 1 \rangle | 1/2, 1/2 \rangle \]

\[ | 3/2, 1/2 \rangle = k | 1, 0 \rangle | 1/2, 1/2 \rangle + \sqrt{\frac{2}{3}} | 1, 1 \rangle | 1/2, -1/2 \rangle \]

\[ | 3/2, -1/2 \rangle = k | 1, 0 \rangle | 1/2, -1/2 \rangle + \sqrt{\frac{2}{3}} | 1, -1 \rangle | 1/2, 1/2 \rangle \]

\[ | 3/2, -3/2 \rangle = | 1, -1 \rangle | 1/2, -1/2 \rangle \]

\[ j = \frac{1}{2} \]

\[ | 1/2, 1/2 \rangle = \sqrt{\frac{2}{3}} | 1, 0 \rangle | 1/2, 1/2 \rangle - \sqrt{\frac{2}{3}} | 1, 1 \rangle | 1/2, -1/2 \rangle \]

\[ | 1/2, -1/2 \rangle = \sqrt{\frac{2}{3}} | 1, 0 \rangle | 1/2, -1/2 \rangle - \sqrt{\frac{2}{3}} | 1, -1 \rangle | 1/2, 1/2 \rangle \]

These states span the same angular momentum space as those given in part a) but are the six basis states of total angular momentum.

d) Prepared with the "good" states for the perturbation, 
\[ H' = \frac{e^2}{8 \pi \epsilon_0 m_e c^2 r^3} \mathbf{L} \cdot \mathbf{S} \], we can now find the expectation in the good states...

\[ < R_{21} | < j, m_j | H' | R_{21} > | j, m_j > = \frac{e^2}{8 \pi \epsilon_0 m_e c^2} < R_{21} | 1/r^3 | R_{21} > < j, m_j | \mathbf{L} \cdot \mathbf{S} | j, m_j > \]

The angular part is \( < j, m_j | \mathbf{L} \cdot \mathbf{S} | j, m_j > = \frac{1}{2} \left[ h^2 (j + 1) - 2 h^2 - \frac{1}{2} \left( \frac{3}{2} + 1 \right) \right] = \frac{1}{2} h^2 \left[ j \cdot (j + 1) - \frac{11}{4} \right] \)

and the radial part -- combining the \( \frac{1}{r^3} \) into the "inner product" from part b) -- is

\[ < R_{21} | 1/r^3 | R_{21} > = \int_0^{\infty} \frac{1}{r^3} < R_{21} | r^2 \cdot r^2 | R_{21} > dr \]

Using \( R_{21}(r) = \sqrt{\frac{1}{24 a^3}} - \frac{r}{2 a} e^{-r/(2a)} \) (Table 4.7 in Griffiths)

\[ \int_0^{\infty} \frac{1}{r^3} R_{21}(r)^2 r^2 dr = \frac{1}{24 a^3} \int_0^{\infty} u \cdot e^{-u} du = \frac{1}{24 a^3} \]

so \( < R_{21} | 1/r^3 | R_{21} > = \frac{1}{24 a^3} \)
Combining all the factors together gives the first-order correction...

\[ E_2^{(1)} = \frac{e^2}{8 \pi \varepsilon_0 m_e c^2} \left( \frac{1}{24 a^3} \right) \left[ -\frac{1}{2} \hbar^2 \left[ j \cdot (j+1) - \frac{11}{4} \right] \right] \]

The \( j = 3/2 \) states has a correction up...

\[ E_2^{(1)} = \frac{e^2 \hbar^2}{384 \pi \varepsilon_0 m_e c^2 a^3} \]

... and the \( j = 1/2 \) has a correction down:

\[ E_2^{(1)} = \frac{e^2 \hbar^2}{192 \pi \varepsilon_0 m_e c^2 a^3} \]

The spin-orbit coupling -- by itself -- breaks the six degenerate \( n=2, l=1 \) hydrogen levels into these two sets of states, according to their total angular momentum.

**QM2)** Given a variational function, the first step is to make sure that it's normalized, since the normalization will undoubtedly depend on the variational parameters. In this case...

\[ \psi_{\text{trial}} = N x e^{-b \cdot x} \]

require normalization

\[ 1 = \int_{0}^{\infty} \psi_{\text{trial}}^2 dx = N^2 \int_{0}^{\infty} x^2 e^{-2 \cdot b \cdot x} dx = \frac{N^2}{4 b^3} \]

\[ N = 2 \cdot b^2 \]

normalized form -- note the complete dependence on \( b \):

\[ \psi_{\text{trial}} = \frac{3}{2} \cdot b^2 \cdot x \cdot e^{-b \cdot x} \]

The next step is to In order to evaluate the expectation  \( \mathcal{E}(b) = \langle \psi_{\text{trial}} | H | \psi_{\text{trial}} \rangle \), with

\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \]

Do the kinetic energy (KE) and the potential energy (PE) parts separately since the potential needs to be broken into it's two spatial domains...
\[ \text{KE term...} \quad \frac{\hbar^2}{2m} \psi = \frac{\hbar^2}{2m} \frac{5}{2b^2} \left[ (b \cdot x - 2) \cdot e^{-b \cdot x} \right] \]

\[ \text{KE(b)} = \int_0^\infty \frac{\hbar^2}{2m} \frac{5}{2b^2} \left[ (b \cdot x - 2) \cdot e^{-b \cdot x} \right] \left( \frac{3}{2b^2} \cdot e^{-b \cdot x} \right) dx = \frac{2 \hbar^2 b^4}{m} \int_0^\infty (2 - b \cdot x) \cdot e^{-2b \cdot x} dx \]

\[ \text{KE term...} \quad \text{PE(b)} = -V_0 \int_0^a \left( \frac{3}{2b^2} \cdot e^{-b \cdot x} \right)^2 dx = -4b^3 \cdot V_0 \int_0^a x \cdot e^{-2b \cdot x} dx \]

Total energy expectation:

\[ E(b) = \frac{2 \hbar^2 b^4}{m} \int_0^\infty (2 - b \cdot x) \cdot e^{-2b \cdot x} dx - 4b^3 \cdot V_0 \int_0^a x \cdot e^{-2b \cdot x} dx \]

Now apply the suggested scaling to more easily handle many of the constants by removing them from the rest of the problem. Use the following substitutions...

\[ z = \frac{x}{a} \quad \beta = b \cdot a \quad \varepsilon = \frac{E}{\hbar^2 \pi^2} \quad v_0 = \frac{V_0}{\hbar^2 \pi^2} \]

...to get

\[ \varepsilon(\beta) = \frac{4 \beta^4}{\pi^2} \int_0^\infty z \cdot (2 - \beta \cdot z) \cdot e^{-2 \beta \cdot z} dz - 4 \beta^3 \cdot v_0 \int_0^1 \left( z \cdot e^{-2 \beta \cdot z} \right)^2 dz \]

Note that, of the original constants \( E, \hbar, m, a, b, V_0 \), only half of them are really needed to specify a unique solution, in this case, \( \varepsilon, v_0, \beta \). The integrals are also easier deal with...

\[ \varepsilon(v_0, \beta) := \left[ \frac{\beta^2}{\pi^2} - v_0 \left[ 1 - \left( 1 + 2 \beta + 2 \beta^2 \right) e^{-2 \beta} \right] \right] \]

For any given situation, evaluate the scaled \( v_0 \), find the minimizing \( \beta \), then translate back to the original values, if necessary. Here's a typical plot for ...
\[ \beta := 0.01 \ldots 4 \]

Note that somewhere between \( v_0 = 0 \) and \( v_0 = 0.5 \) there fails to be a minimum energy below zero. This means that, at least for this trial wavefunction, there is no bound state solution.

To find the threshold of the bound state more precisely, home in on the value for \( v_0 \) that just dips below \( \epsilon = 0 \). The plot below shows the function \( \epsilon(\beta) \) for \( v_0 \) values bracketing the threshold.

\[ \beta := 0.001 \ldots 1 \]

No bound solution occurs until \( v_0 \sim 0.2980 \).

The exact (non variational) result is \( v_0 = \frac{1}{4} \) so the actual threshold is in a slightly shallower well than that predicted by the variational solution.
Here’s a blow-up of the minimum for the case of $v_0 = 1...$ 

This has a minimum at approximately $\beta \approx 1.79$ where $\varepsilon \approx -0.369$

$\beta = 1.79 \quad \varepsilon = -0.369$

Exact result: $\varepsilon = -0.457...$ is slightly more bound (lower energy) than the approximate ground state solution, as must be the case.

In terms of the original problem as specified, the variational result proves that

1. There will be bound at least one state if $V_0 > 0.298 \frac{\hbar^2 \cdot \pi^2}{2 \cdot m \cdot a^2}$

2. If $V_0 = \frac{\hbar^2 \cdot \pi^2}{2 \cdot m \cdot a^2}$, then the ground state energy should be $E_0 < -0.369 \frac{\hbar^2 \cdot \pi^2}{2 \cdot m \cdot a^2}$

A more flexible trial wavefunction would further restrict these bounds. When added flexibility fails to reduce the energy, the you can be confident in its value -- without ever solving Schrödinger's equation.