Problem 11.1

(a) The Hamiltonian can be rewritten as

\[ \hat{H} = \sqrt{(m_e c^2)^2 + c^2 |\hat{p}|^2} - \frac{Ze^2}{4\pi\epsilon_0 |r|} = \sqrt{(m_e c^2)^2 + c^2 \hat{p}_r^2 + \frac{c^2 |\hat{L}|^2}{r^2}} - \frac{Ze^2}{4\pi\epsilon_0 |r|} \]

recall Eq.(29.56) in HSO

\[ |\hat{L}|^2 = -\hbar r^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right] \]

Since \(|\hat{L}|^2\) has no \(r\) dependence, \(\hat{H}\) is basically just a function of \(|\hat{L}|^2\) and hence \(|\hat{L}|^2\) commutes with \(\hat{H}\). The expression for \(\hat{L}_z\) is

\[ \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \]

Again \(\hat{L}_z\) has no \(r\) dependence, and it is easy to verify that \(\hat{L}_z\) and \(|\hat{L}|^2\) commute. Therefore, \(\hat{L}_z\) commutes with any function of \(|\hat{L}|^2\), including \(\hat{H}\).

(b) A solution \(\psi\) to the deBroglie equation also satisfies

\[ (E - V(r))^2 \psi = \left[ (m_e c^2)^2 + c^2 |\hat{p}|^2 \right] \psi = \left[ (m_e c^2)^2 + c^2 \hat{p}_r^2 + \frac{c^2 |\hat{L}|^2}{r^2} \right] \psi \]

We assume a solution of the form

\[ \psi = r^s e^{-\beta r} \]

Since the assumed \(\psi\) has no \(\theta\) nor \(\phi\) dependence, we have

\[ \left[ (m_e c^2)^2 + c^2 \hat{p}_r^2 + \frac{c^2 |\hat{L}|^2}{r^2} \right] \psi = \left[ (m_e c^2)^2 + c^2 \hat{p}_r^2 \right] \psi = \left[ m_e^2 c^4 - \hbar^2 c^2 \beta^2 + \frac{2\hbar^2 c^2 \beta (s + 1)}{r} - \frac{\hbar^2 c^2 s(s + 1)}{r^2} \right] \psi \]

(2)
where we have used the following equation in obtaining the above results

$$\hat{p}_r = -\frac{\hbar}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

The left-hand side of Eq.(1) gives

$$[E^2 - 2EV + V^2] \psi = \left[ E^2 + \frac{2Ze^2E}{4\pi\epsilon_0r} + \frac{Z^2e^4}{16\pi^2\epsilon_0r^2} \right] \psi \quad (3)$$

Matching terms in Eq.(3) with those in Eq.(2) gives

$$m_e^2c^4 - \hbar^2\beta^2c^2 = E^2 \quad (4)$$

$$\hbar^2c^2\beta(s+1) = \frac{Ze^2E}{4\pi\epsilon_0} \quad (5)$$

$$\hbar^2c^2s(s+1) = -\frac{Z^2e^4}{16\pi^2\epsilon_0} \quad (6)$$

From Eq.(5) we obtain

$$\beta = \frac{Ze^2E}{4\pi\epsilon_0\hbar^2c^2(s+1)}$$

Substituting the above equation into Eq.(4), we arrive at

$$E = \frac{m_e^2c^2}{\sqrt{1 + (\alpha Z)^2/(s+1)^2}} \approx m_e^2c^2\sqrt{1 - (\alpha Z)^2/(s+1)^2}$$

where $\alpha$ is the fine structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$$

We solve for $s$ from Eq.(6) to be

$$s = \frac{-1 + \sqrt{1 - 4(\alpha Z)^2}}{2}$$

(c) If we neglect $s$ and make it zero, the result obtained in the last part is equal to what would be obtained from the solution of the Dirac equation

$$E_{1s} = m_e^2c^2\sqrt{1 - (\alpha Z)^2}$$
Problem 11.2

(a) The 1s and 2p states do not possess a dipole moment due to their symmetry with respect to the three coordinates. The dipole moment for the superposition state is

\[-e\langle \Psi | r | \Psi \rangle = \frac{-e}{2} \left[ \langle \psi_{100} | r | \psi_{100} \rangle + \langle \psi_{210} | r | \psi_{210} \rangle + \langle \psi_{100} | r | \psi_{210} \rangle \left( e^{-i(E_2 - E_1) t/\hbar} + e^{-i(E_1 - E_2) t/\hbar} \right) \right] \]

\[= -ea_H \sqrt{\frac{1}{3}} \left( \frac{32}{27} \right)^{3/2} \hat{k} \]

where we have made use of Eq.(30.27) in HSO.

(b) We know from the selection rule that \( \psi_{320} \) does not decay to \( \psi_{100} \) under the dipole approximation as the difference in the \( l \) value is 2.

(c) The 1s state is spherically symmetric and therefore the 2p\(_x\), 2p\(_y\), and 2p\(_z\) states all have the same decay rate to 1s.

(d) The 2p\(_y\) state would radiate in such a way that the electric field at \( r = iR \) is \( y \)-directed. The 2p\(_y\) state is a superposition of two \( \psi_{nlm} \) states

\[\psi_{2p_y} = \psi_{211} + \psi_{21-1} \]

\[\psi_{211} = \frac{1}{2i} \left( r e^{-r/2a_\mu} \sin \theta \sin \phi \right) \]

\[\psi_{21-1} = \frac{1}{8 \sqrt{\pi a_\mu^3}} \left( r e^{-r/2a_\mu} \sin \theta \sin \phi \right) \]

(e) \( \psi_{100} \) has a sphere shape while \( \psi_{211} \) has a donut shape with phase \( e^{i\phi} \). The superposition of the two would be bigger on the side that is in phase and smaller on the other side that is out of phase. The charge distribution on the x-y plane is depicted at four time instants in the following graphs and it rotates around the z axis:
charge distribution at time $t=0$

$x$ (plot to proportion but the unit randomly chosen)
charge distribution at time $t = \pi \hbar / 2 \left( E_2 - E_1 \right)$
charge distribution at time $t = \frac{\pi \hbar}{E_2 - E_1}$
The energy expectation can be computed directly

\[
\langle \hat{H} \rangle = \frac{1}{2} \left[ \langle \psi_{100} | \hat{H} | \psi_{100} \rangle + \langle \psi_{211} | \hat{H} | \psi_{211} \rangle \right] = \frac{E_1 + E_2}{2} = -\frac{5}{8} I_\mu
\]

where we have made use of the following identity

\[
\langle \psi_{100} | \psi_{211} \rangle = 0
\]

since

\[
\langle Y_{lm} | Y_{l'm'} \rangle = \delta_{ll'} \delta_{mm'}
\]
Problem 11.3

(a) The reduced mass is

\[ \mu = \frac{m_e \cdot m_e}{m_e + m_e} = \frac{m_e}{2} \]

which is about half of that for the hydrogen atom. The ground-state energy is

\[ E = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \]

which is higher than the ground-state energy for the hydrogen atom. The size of the ground-state orbital is characterized by \( a_\mu \) (Eq.(29.28) in HSO):

\[ \frac{1}{a_\mu} = \frac{\mu e^2}{4\pi \epsilon_0 \hbar^2} \]

Since the reduced mass is decreased by a factor of 2, the orbital size is increased by a factor of 2.

(b) The average distance is from Eq.(30.16) in HSO

\[ \langle \psi_{43m}|r|\psi_{43m} \rangle = \frac{a_\mu}{2} \left[ 3n^2 - l(l+1) \right] = 18a_\mu \]

(c) The decay rate is proportional to:

\[ \gamma \propto \omega^3 |\langle \psi_{1s}|r|\psi_{2p} \rangle|^2 \]

The orbitals are scaled by a factor of 2, so the matrix element squared is scaled by a factor of 4. The energy scaled by a factor of 1/2, so \( \omega^3 \) is scaled by a factor of 1/8 from the hydrogen atom. Therefore the decay rate is half of that for the hydrogen atom and from Eq.(30.81) we know it is

\[ \gamma = 3.13 \times 10^8 \text{ sec}^{-1} \]

(d) For momentum to be conserved in such a process, two photons are emitted in opposite directions when electron-positron annihilation occurs.

Problem 11.4

The ground state energy of the negative hydrogen ion can be estimated from Eq.(31.24) in HSO (note that there is a factor of 2 missing) with \( Z = 1 \) and it turns out to be greater than that of the hydrogen atom.
\[ E_{\text{min}} = -2 \left[ Z - \frac{5}{16} \right]^2 I_H = -2 \frac{9^2}{16^2} I_H = -8.6 \text{eV} > -I_H = -13.6 \text{eV} \]

In reality though the ground state energy of a negative hydrogen ion is \(-14.35 \text{eV}\) which is smaller than that of the hydrogen atom \(I_H = -13.6 \text{eV}\) and the negative hydrogen ion is stable. The independent particle assumption happens to not work well for this problem and the variational estimate is not so great in this case.

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**Problem 11.5**

From Eq.(31.55) in HSO the trial wavefunction for the 1s\(^2\)\(^1\)S ground state is

\[ \Psi_t^{1s^2\text{ }^1S} = \phi_{1s}(r_1 : \eta)\phi_{1s}(r_2 : \eta) \frac{\chi_1(\sigma_1)\chi_1(\sigma_2) - \chi_1(\sigma_2)\chi_1(\sigma_1)}{\sqrt{2}} \]

where \(\eta\) is given by Eq.(31.23) in HSO

\[ \eta = Z - \frac{5}{16} = \frac{27}{16} = 1.6875 \]

The trial wavefunction for the 1s2s \(^1\)S singlet state is

\[ \Psi_t^{1s2s\text{ }^1S} = \left[ \phi_{1s}(r_1 : \eta_1)\phi_{2s}(r_2 : \eta_2) + \phi_{2s}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_1) \right] \frac{\chi_1(\sigma_1)\chi_1(\sigma_2) - \chi_1(\sigma_2)\chi_1(\sigma_1)}{\sqrt{2}} \]

where \(\eta_1\) and \(\eta_2\) are given by the screening argument in Sec.(31.4) in HSO:

\[ \eta_1 \approx Z - 2 \]

\[ \eta_2 \approx Z - 1 = 1 \]

The trial wavefunctions for the 1s2s \(^3\)S triplet states are

\[ \Psi_t^{1s2s\text{ }^3S\text{ }M_S=1} = \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2s}(r_2 : \eta_2) - \phi_{2s}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_1)}{\sqrt{2}} \chi_1(\sigma_1)\chi_1(\sigma_2) \]

\[ \Psi_t^{1s2s\text{ }^3S\text{ }M_S=0} = \left[ \phi_{1s}(r_1 : \eta_1)\phi_{2s}(r_2 : \eta_2) - \phi_{2s}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_1) \right] \frac{\chi_1(\sigma_1)\chi_1(\sigma_2) + \chi_1(\sigma_2)\chi_1(\sigma_1)}{\sqrt{2}} \]

\[ \Psi_t^{1s2s\text{ }^3S\text{ }M_S=-1} = \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2s}(r_2 : \eta_2) - \phi_{2s}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_1)}{\sqrt{2}} \chi_1(\sigma_1)\chi_1(\sigma_2) \]

Selection rule tells us that the 2s state does not radiatively decay to the 1s state, and therefore the 1s2s singlet and triplet states do not radiatively decay to the ground state.

The trial wavefunction for the 1s2p \(^1\)P singlet state is
\[ \psi_{t}^{1s2p \, 1P} = \left[ \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2p}(r_2 : \eta_2) + \phi_{2p}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_1)}{\sqrt{2}} \right] \left[ \frac{\chi_1(\sigma_1)\chi_1(\sigma_2) - \chi_1(\sigma_2)\chi_1(\sigma_1)}{\sqrt{2}} \right] \]

To calculate the radiative decay rate we need to compute the dipole:

\[ \langle \psi_{t}^{1s2s \, 1S}|r_1+r_2|\psi_{t}^{1s2p \, 1P} \rangle = \frac{1}{\sqrt{2}} \left[ \langle \phi_{1s}(r_1 : \eta)|\phi_{2p}(r_2 : \eta)\rangle|r_1 + r_2|\phi_{2p}(r_1 : \eta_2)\rangle + \langle \phi_{2p}(r_1 : \eta)|\phi_{1s}(r_2 : \eta_2)\rangle|r_2|\phi_{1s}^*(r_2 : \eta_2)\rangle \right] \]

\[ = \frac{1}{\sqrt{2}} \left[ \langle \phi_{1s}(r_1 : \eta)|\phi_{2p}(r_1 : \eta_2)\rangle + \langle \phi_{1s}(r_1 : \eta)|\phi_{2p}(r_2 : \eta_2)\rangle \right] \]

\[ = \sqrt{2}\langle \phi_{1s}(r : \eta)|\phi_{2p}(r : \eta_2)\rangle \]

According to Eq.(30.27) in HSO, the above matrix element is proportional to

\[ \int_{0}^{\infty} P_{21}^r(r : \eta_2)rP_{10}(r : \eta)dr = \int_{0}^{\infty} \frac{1}{2} \sqrt{\frac{\eta_2}{a_\mu}} \left( \frac{r\eta_2}{a_\mu} \right)^2 e^{-r\eta_2/2a_\mu} \cdot 2 \sqrt{\frac{\eta_2}{a_\mu}} e^{-\eta_2/2a_\mu} dr = \frac{313.535\eta_1^{1.5}\eta_2^{2.5}}{(2\eta + \eta_2)^5} \]

where the above integral is carried out by using the following two commands in Mathematica (each one of them is supposed to be in one line, but separated due to space limit in this document)

```
Integrate[Subscript[\[Eta], 2]^-0.5/2/(6 a)^-0.5 (r Subscript[\[Eta], 2]/a)^-2 \nExp[-r Subscript[\[Eta], 2]/a] r 2 \[\[Eta]/a]^-0.5 r \[\[Eta]/a] Exp[-\[\[Eta]/a] r/a] \n, \{r, 0, Infinity\}]
```

```
Simplify[\%, \{\[\[Eta]\], \[\Element\] Reals, \nSubscript[\[\[Eta]\], 2] \[\Element\] Reals, \[\[\[Eta]\] > 0, \nSubscript[\[\[\[Eta]\], 2] > 0, a \[\Element\] Reals, \na > 0\}]]
```

Therefore the dipole moment squared is scaled from that for the hydrogen atom by

\[ \frac{2\eta^3\eta_2^5}{(2\eta + \eta_2)^{10}/2} \]

The frequency \( \omega \) is scaled by \( Z = 2 \) from that of the hydrogen atom. Altogether the decay rate can be obtained from scaling the decay rate for the hydrogen atom Eq.(30.81) in HSO to be

\[ 6.26 \times 10^8 \times 2 \times 1.6875^3/(1.6875 \times 2 + 1)^{10} \times 2^3 = 5.53 \times 10^8 \text{sec}^{-1} \]

The trial wavefunctions for the 1s2p \( 3P \) triplet states are

\[ \psi_{t}^{1s2p \, 3P \, M_S=1} = \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2p}(r_2 : \eta_2) - \phi_{2p}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_2)}{\sqrt{2}} \chi_{1}(\sigma_1)\chi_{1}(\sigma_2) \]
\[ \psi_t^{1s2p\,^3P\,M_S=0} = \left[ \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2p}(r_2 : \eta_2) - \phi_{2p}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_2)}{\sqrt{2}} \right] \sqrt{\chi_1(\sigma_1)\chi_1(\sigma_2) + \chi_1(\sigma_2)\chi_1(\sigma_1)} \]

\[ \psi_t^{1s2p\,^3P\,M_S=-1} = \frac{\phi_{1s}(r_1 : \eta_1)\phi_{2p}(r_2 : \eta_2) - \phi_{2p}(r_1 : \eta_2)\phi_{1s}(r_2 : \eta_2)}{\sqrt{2}} \chi_1(\sigma_1)\chi_1(\sigma_2) \]

It is easy to see that the triplet spin functions are orthogonal to the ground-state spin function and hence there will be no radiative decay from the triplet states to the ground-state.

---

Problem 11.6

Similar to section 31.7 in HSO, we obtain the energy estimates for the \(1s3d\,^1D\) state

\[ E_{1s3d\,^1D} = I[1s] + I[3d] + D[1s, 3d] + E[1s, 3d] \]

and for the triplet states

\[ E_{1s3d\,^3D} = I[1s] + I[3d] + D[1s, 3d] - E[1s, 3d] \]

The \(I\) terms can be computed from Eq.(31.32) in HSO to be

\[ I[1s] = 4I_H - 8I_H = -4I_H \]

\[ I[3d] = \frac{1}{9}I_H - \frac{4}{9}I_H = -0.3333I_H \]

Using the following identities

\[ a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_ee^2} \]

\[ I_H = \frac{m_ee^4}{32\pi^2\epsilon_0^2\hbar^2} = \frac{\hbar^2}{2m_ea_0^2} = \frac{1}{2} e^2 \frac{1}{4\pi\epsilon_0 a_0} \]

\[ P_{1s}(r) = 2\sqrt{\frac{n_1}{a_0}} \frac{\eta_1}{a_0} e^{-rn/a_0} \]

\[ P_{3d}(r) = \frac{4}{81\sqrt{30}} \sqrt{\frac{n_3}{a_0}} \left( \frac{n_3r}{a_0} \right)^3 e^{-n_3r/3a_0} \]

We rewrite the \(D[1s, 3d]\) and \(E[1s, 3d]\) integrals to be

\[ D[1S, 3d] = I_H \frac{8 \cdot 16}{812 \cdot 30} \eta_1^2 \eta_3^2 \int_0^{\infty} dr \left( \int_0^r r s^6 e^{-2rn-2n_3s/3} ds + \int_r^{\infty} r^2 s^5 e^{-2rn-2n_3s/3} ds \right) \]

The above integral can be carried out by Mathematica:
Integrate[
  Integrate[
    s^6 r \text{Exp}[-2 r \text{Subscript}[\eta, 1] - 2 \text{Subscript}[\eta, 3] s/3], {s, 0, r}]
  + Integrate[
    s^5 r^2 \text{Exp}[-2 r \text{Subscript}[\eta, 1] - 2 \text{Subscript}[\eta, 3] s/3], {s, r, \infty}], {r, 0, \infty}
]

Simplify[%, \{\text{Subscript}[\eta, 1] \in \text{Reals}, \text{Subscript}[\eta, 3] \in \text{Reals}, \text{Subscript}[\eta, 1] > 0, \text{Subscript}[\eta, 3] > 0\}]

and we obtain

\[ D[1s, 3d] = I_H \cdot \frac{8 \cdot 16 \cdot 5 \cdot 81}{812 \cdot 30 \cdot \eta_1^3 \eta_3^7} \int_0^\infty dr \left[ \int_0^r r s^6 e^{-\left(\eta_1 + 2\eta_3 / 3\right)(r+s)} ds + \int_r^\infty r^6 s e^{-\left(\eta_1 + 2\eta_3 / 3\right)(r+s)} ds \right] \]

\[
= 0.2222154763 I_H
\]

similarly for the \(E[1s, 3d]\) integral:

\[ E[1S, 3d] = I_H \cdot \frac{8 \cdot 16 \cdot 5 \cdot 81}{812 \cdot 150 \cdot \eta_1^3 \eta_3^7} \int_0^\infty dr \left[ \int_0^r r s^6 e^{-\left(\eta_1 + 2\eta_3 / 3\right)(r+s)} ds + \int_r^\infty r^6 s e^{-\left(\eta_1 + 2\eta_3 / 3\right)(r+s)} ds \right] \]

Mathematica commands

Integrate[
  Integrate[
    s^6 r \text{Exp}[-(\text{Subscript}[\eta, 1] + \text{Subscript}[\eta, 3]/3)(s + r)], \{s, 0, r\}]
  + Integrate[
    s r^6 \text{Exp}[-(\text{Subscript}[\eta, 1] + \text{Subscript}[\eta, 3]/3)(s + r)], \{s, r, \infty}\}, \{r, 0, \infty\}\]

Simplify[%, \{\text{Subscript}[\eta, 1] \in \text{Reals}, \text{Subscript}[\eta, 3] \in \text{Reals}, \text{Subscript}[\eta, 1] > 0, \text{Subscript}[\eta, 3] > 0\}]

\[ E[1s, 3d] = I_H \cdot \frac{8 \cdot 16 \cdot 5 \cdot 81}{812 \cdot 30 \cdot \eta_1^3 \eta_3^7} \frac{7971615}{8(3\eta_1 + \eta_3)^9} = 0.00002569287053 I_H \]
Altogether we obtain

\[ E[1s3d^1D] = -4.1110921642I_H \]

\[ E[1s3d^3D] = -4.1111435499I_H \]