HW #11

1. Fine-structure of the hydrogen atom

We use the 2s wave function

$$R_{2s} = (2a)^{-3/2} \left(2 - \frac{r}{a}\right) E^{-r/(2a)}$$

$$\frac{e^{-\frac{r}{2a}} \left(2 - \frac{r}{a}\right)}{2\sqrt{2}\, a^{3/2}}$$

The full wave function is

$$\psi_{2s} = \frac{1}{\sqrt{4\pi}} R_{2s}$$

$$\frac{e^{-\frac{r}{2a}} \left(2 - \frac{r}{a}\right)}{4\, a^{3/2} \sqrt{2\pi}}$$

Here, $a = a_0 / Z = \hbar^2 / (Z e^2 m)$. Similarly,

$$R_{2p} = (2a)^{-3/2} \frac{r}{\sqrt{3}\, a} E^{-r/(2a)}$$

$$\frac{e^{-\frac{r}{2a}}\, r}{2\sqrt{6}\, a^{5/2}}$$

As a preparation for calculating the spin-orbit interaction, $\vec{L}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right) = \frac{\hbar^2}{2}\,(j(j+1) - l(l+1) - s(s+1))$.
For $j = l + \frac{1}{2}$,
$\vec{L}\cdot\vec{S} = \frac{\hbar^2}{2}\,((l+\frac{1}{2})(l+\frac{3}{2}) - l(l+1) - \frac{3}{4}) = \frac{\hbar^2}{2}\, l$,
while for $j = l - \frac{1}{2}$,
$\vec{L}\cdot\vec{S} = \frac{\hbar^2}{2}\,((l-\frac{1}{2})(l+\frac{1}{2}) - l(l+1) - \frac{3}{4}) = -\frac{\hbar^2}{2}\,(l+1)$,
For the calculations of the relativistic corrections, we use the fact that
$-\frac{1}{8 m^3 c^2}\left\langle\left(\vec{p}^2\right)^2\right\rangle = \left\langle(-\hbar^2\,\Delta)^2\right\rangle = -\frac{\hbar^4}{8 m^3 c^2}\int d^3 x\, \psi^*\, \Delta\Delta\psi = \hbar^4 \int d^3 x (\Delta\psi)^*\,(\Delta\psi)$
$= -\frac{\hbar^4}{8 m^3 c^2}\int d^3 x\left(\frac{d^2}{d r^2} + \frac{2}{r}\,\frac{d}{d r} - \frac{l(l+1)}{r^2}\right)(R\, Y_l{}^m)^*\left(\frac{d^2}{d r^2} + \frac{2}{r}\,\frac{d}{d r} - \frac{l(l+1)}{r^2}\right)(R\, Y_l{}^m)$
$= -\frac{\hbar^4}{8 m^3 c^2}\int r^2\, d r\left(\frac{d^2}{d r^2} + \frac{2}{r}\,\frac{d}{d r} - \frac{l(l+1)}{r^2}\right) R(r)\left(\frac{d^2}{d r^2} + \frac{2}{r}\,\frac{d}{d r} - \frac{l(l+1)}{r^2}\right) R(r)$.
The Darwin term for the Coulomb potential is proportional to $\Delta V_c = \Delta\,\frac{-Z e^2}{r} = 4\pi Z e^2\,\delta(\vec{x}) = 4\pi\,\frac{\hbar^2}{m a}\,\delta(\vec{x})$

2s

First, the releativistic correction:

```
Integrate[-ħ^4/(8 m^3 c^2) (D[R2s, {r, 2}] + 2/r D[R2s, r])^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$$-\frac{13\,\hbar^4}{128\,a^4\,c^2\,m^3}$$

Second, the spin-orbit interaction. Because $L = 0$, it identically vanishes.

Third, the Darwin term.

```
ħ^2/(8 m^2 c^2) 4 π ħ^2/(m a) ψ2s^2 /. {r → 0}
```

$$\frac{\hbar^4}{16\,a^4\,c^2\,m^3}$$

```
% + %%
```

$$-\frac{5\,\hbar^4}{128\,a^4\,c^2\,m^3}$$

$2\,p_{1/2}$

First, the relativistic correction,

```
Integrate[-ħ^4/(8 m^3 c^2) (D[R2p, {r, 2}] + 2/r D[R2p, r] - 2/r^2 R2p)^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$$-\frac{7\,\hbar^4}{384\,a^4\,c^2\,m^3}$$

Second, the spin-orbit interaction.

```
Integrate[g/(4 m^2 c^2) 1/r^3 ħ^2/(m a) (-ħ^2) R2p^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$$-\frac{g\,\hbar^4}{96\,a^4\,c^2\,m^3}$$

Third, the Darwin term. Because the wave function vanishes at the origin, it is identically zero.

```
% + %% /. {g → 2}
```

$$-\frac{5\,\hbar^4}{128\,a^4\,c^2\,m^3}$$

$2\,p_{3/2}$

First, the relativistic correction. We use the fact that $\vec{p}^{\,2}\,\psi = -\hbar^2\,Y_1{}^m\left(\frac{d^2}{d\,r^2} + \frac{2}{r}\,\frac{d}{d\,r} - \frac{2}{r^2}\right)R$,

```
Integrate[-ħ^4/(8 m^3 c^2) (D[R2p, {r, 2}] + 2/r D[R2p, r] - 2/r^2 R2p)^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$$-\frac{7\,\hbar^4}{384\,a^4\,c^2\,m^3}$$

Second, the spin-orbit interaction.

```
Integrate[g/(4 m^2 c^2) 1/r^3 ħ^2/(m a) ħ^2/2 R2p^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$$\frac{g\,\hbar^4}{192\,a^4\,c^2\,m^3}$$

Third, the Darwin term. Because the wave function vanishes at the origin, it is identically zero.

```
% + %% /. {g → 2}
```

$$-\frac{\hbar^4}{128\,a^4\,c^2\,m^3}$$

Therefore, the $2\,s$ and $2\,p_{1/2}$ states are still degenerate, and have the energy $\frac{-e^2}{8\,a} - \frac{5\,\hbar^4}{128\,a^4\,m^3\,c^2} = \frac{-e^2}{a}\,(\frac{1}{8} + \frac{5}{128}\,\alpha^2)$, while the $2\,p_{3/2}$ states have the energy
$\frac{-e^2}{a}\,(\frac{1}{8} + \frac{1}{128}\,\alpha^2)$,
where $a = \frac{e^2}{\hbar\,c}$.

2. Harmonic oscillator

Exact result

The ground-state wave function is

```
ψ0 = (m ω/(π ħ))^(1/4) E^(-m ω x^2/(2 ħ))
```

$$\frac{e^{-\frac{m\,x^2\,\omega}{2\,\hbar}}\,\left(\frac{m\,\omega}{\hbar}\right)^{1/4}}{\pi^{1/4}}$$

```
Simplify[Series[ψ0 /. {ω → ω Sqrt[1 + ϵ]}, {ϵ, 0, 2}]]
```

$$\frac{e^{-\frac{m\,x^2\,\omega}{2\,\hbar}}\,\left(\frac{m\,\omega}{\hbar}\right)^{1/4}}{\pi^{1/4}} + \frac{e^{-\frac{m\,x^2\,\omega}{2\,\hbar}}\,\left(\frac{m\,\omega}{\hbar}\right)^{1/4}\,(-2\,m\,x^2\,\omega + \hbar)\,\epsilon}{8\,\pi^{1/4}\,\hbar} + \frac{e^{-\frac{m\,x^2\,\omega}{2\,\hbar}}\,\left(\frac{m\,\omega}{\hbar}\right)^{1/4}\,(4\,m^2\,x^4\,\omega^2 + 4\,m\,x^2\,\omega\,\hbar - 7\,\hbar^2)\,\epsilon^2}{128\,\pi^{1/4}\,\hbar^2} + O[\epsilon]^3$$

Perturbative result

We need to know the matrix elements. Using $V = \frac{1}{2}\epsilon m \omega^2 x^2 = \epsilon \frac{\hbar\omega}{4}(a + a^\dagger)^2$.
$V_{00} = \epsilon \frac{\hbar\omega}{4} \left\langle 0 \middle| (a+a^\dagger)^2 \middle| 0 \right\rangle = \epsilon \frac{\hbar\omega}{4}$,
$V_{20} = \epsilon \frac{\hbar\omega}{4} \left\langle 0 \middle| (a+a^\dagger)^2 \middle| 2 \right\rangle = \epsilon \frac{\hbar\omega}{4} \sqrt{2}$,
$V_{22} = \epsilon \frac{\hbar\omega}{4} \left\langle 2 \middle| (a+a^\dagger)^2 \middle| 2 \right\rangle = \epsilon \frac{\hbar\omega}{4} (3+2)$,
$V_{42} = \epsilon \frac{\hbar\omega}{4} \left\langle 2 \middle| (a+a^\dagger)^2 \middle| 4 \right\rangle = \epsilon \frac{\hbar\omega}{4} \sqrt{12}$.
We use Eq. (5.1.44) in Sakurai.

$$|0\rangle = |0^{(0)}\rangle + |2^{(0)}\rangle \frac{V_{20}}{E_0^{(0)} - E_2^{(0)}} + |4^{(0)}\rangle \frac{V_{42}\, V_{20}}{(E_0^{(0)} - E_2^{(0)})(E_0^{(0)} - E_4^{(0)})}$$
$$+ |2^{(0)}\rangle \frac{V_{22}\, V_{20}}{(E_0^{(0)} - E_2^{(0)})(E_0^{(0)} - E_2^{(0)})} - |2^{(0)}\rangle \frac{V_{00}\, V_{20}}{(E_0^{(0)} - E_2^{(0)})^2}$$

$$= |0^{(0)}\rangle - |2^{(0)}\rangle \frac{\epsilon}{4\sqrt{2}} + |4^{(0)}\rangle \frac{\epsilon^2 \sqrt{6}}{64}$$
$$+ |2^{(0)}\rangle \frac{\epsilon^2\, 5}{32\sqrt{2}} - |2^{(0)}\rangle \frac{\epsilon^2}{32\sqrt{2}}$$
$$= |0^{(0)}\rangle - |2^{(0)}\rangle \frac{\epsilon}{4\sqrt{2}} + |4^{(0)}\rangle \frac{\epsilon^2 \sqrt{6}}{64}$$
$$+ |2^{(0)}\rangle \frac{\epsilon^2}{8\sqrt{2}}$$

This state is not normalized, and it needs to be renormalized by
$Z^{-1} = \langle 0 | 0 \rangle = 1 + \frac{\epsilon^2}{32} + O(\epsilon^4)$.
On the other hand,using (A.4.3) and (A.4.5) in Sakurai,

$$\psi_2 = \frac{1}{\sqrt{2}} \left(\frac{2\, m\, \omega\, x^2}{\hbar} - 1 \right) \left(\frac{m\, \omega}{\pi\, \hbar} \right)^{1/4} E^{-m\,\omega\, x^2/(2\,\hbar)}$$

$$\frac{e^{-\frac{m x^2 \omega}{2\hbar}} \left(-1 + \frac{2 m x^2 \omega}{\hbar}\right) \left(\frac{m\omega}{\hbar}\right)^{1/4}}{\sqrt{2}\, \pi^{1/4}}$$

$$\psi_4 = \frac{1}{2\sqrt{6}} \left(4 \left(\frac{m\, \omega\, x^2}{\hbar} \right)^2 - 12 \frac{m\, \omega\, x^2}{\hbar} + 3 \right) \left(\frac{m\, \omega}{\pi\, \hbar} \right)^{1/4} E^{-m\,\omega\, x^2/(2\,\hbar)}$$

$$\frac{e^{-\frac{m x^2 \omega}{2\hbar}} \left(3 + \frac{4 m^2 x^4 \omega^2}{\hbar^2} - \frac{12 m x^2 \omega}{\hbar}\right) \left(\frac{m\omega}{\hbar}\right)^{1/4}}{2\sqrt{6}\, \pi^{1/4}}$$

$$\mathbf{Simplify}\left[\mathbf{Series}\left[\left(1 - \frac{\epsilon^2}{64}\right)\left(\psi_0 - \frac{\epsilon}{4\sqrt{2}}\psi_2 + \frac{\epsilon^2\sqrt{6}}{64}\psi_4 + \frac{\epsilon^2}{8\sqrt{2}}\psi_2\right), \{\epsilon, 0, 2\}\right]\right]$$

$$\frac{e^{-\frac{m x^2 \omega}{2\hbar}} \left(\frac{m\omega}{\hbar}\right)^{1/4}}{\pi^{1/4}} + \frac{e^{-\frac{m x^2 \omega}{2\hbar}} \left(\frac{m\omega}{\hbar}\right)^{1/4} (-2\, m\, x^2\, \omega + \hbar)\, \epsilon}{8\, \pi^{1/4}\, \hbar} +$$
$$\frac{e^{-\frac{m x^2 \omega}{2\hbar}} \left(\frac{m\omega}{\hbar}\right)^{1/4} (4\, m^2\, x^4\, \omega^2 + 4\, m\, x^2\, \omega\, \hbar - 7\, \hbar^2)\, \epsilon^2}{128\, \pi^{1/4}\, \hbar^2} + O[\epsilon]^3$$

It agrees with the expansion of the exact result.

3. Magnetic Field

We use the MKSA system. The Hamiltonian of the electron in the magnetic field is written in the symmetric gauge where $\vec{A} = \frac{B}{2}(-y, x, 0)$,

$H = \frac{(\vec{p}-e\vec{A})^2}{2m} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} - g\frac{e}{2m}\vec{s}\cdot\vec{B}$

$= \frac{1}{2m}((p_x + eBy/2)^2 + (p_y - eBx/2)^2 + p_z{}^2) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} - g\frac{eB}{2mc}s_z$

$= \frac{1}{2m}\left(\vec{p}^2 + eB(p_x y - p_y x) + \frac{e^2B^2}{4}(x^2+y^2)\right) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} - g\frac{e\hbar B}{2mc}m_s$

$= \frac{1}{2m}\left(\vec{p}^2 - eBL_z + \frac{e^2B^2}{4}(x^2+y^2)\right) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} - g\frac{e\hbar B}{2mc}m_s.$

The last term is already diagonalized for $m_s = \pm\frac{1}{2}$.

At $O(B)$, the correction from the second term in the parenthesis vanishes because $L_z = 0$. At $O(B^2)$, the last term in the parentheses contributes.

```
R1s = a^-3/2 2 E^-r/a
```

$\frac{2\,e^{-\frac{r}{a}}}{a^{3/2}}$

Because of the isotropy of the wave function, we can replace $x^2 + y^2 \to \frac{2}{3}r^2$

```
Integrate[(e^2 B^2)/(8 m) 2/3 r^2 R1s^2 r^2, {r, 0, ∞}, Assumptions → a > 0]
```

$\frac{a^2 B^2 e^2}{4\,m}$

Another possible contribution at $O(B^2)$ coming from the second-order in the $O(B)$ operator again vanishes because $L_z = 0$. Therefore, the correction up to the second order,

$\Delta E = -g\frac{e\hbar B}{2m}m_s + a^2\frac{e^2B^2}{4m}.$

$\frac{1}{\mu_0} + n a^2 \frac{e^2}{4m} = \frac{1}{\mu_0} + n a^2 a \frac{me^2}{4\pi\epsilon_0\hbar^2}\frac{e^2}{4m} = \frac{1}{\mu_0} + n a^3 \frac{e^4}{16\pi\epsilon_0\hbar^2}$

$= \frac{1}{\mu_0}\left(1 + n a^3 \frac{e^4\mu_0}{16\pi\epsilon_0\hbar^2}\right) = \frac{1}{\mu_0}\left(1 + n a^3 \frac{e^4}{16\pi\epsilon_0{}^2\hbar^2c^2}\right) = \frac{1}{\mu_0}(1 + n a^3 \pi\alpha^2)$

4. Index of Refraction

Sakurai quotes the polarizability of the hydrogen atom $\alpha = \frac{9}{2} a_0{}^3$ (5.1.73), where a_0 is the Bohr radius. Note that this result is in the Gaussian unit. In the MKSA unit, the only modification is the energy levels from $\frac{e^2}{2 a_0} \frac{1}{n^2}$ to $\frac{1}{4\pi\epsilon_0} \frac{e^2}{2 a_0} \frac{1}{n^2}$, and hence the polarizability becomes $\alpha = 4\pi\epsilon_0 \frac{9}{2} a_0{}^3$. The energy density of the electric field is $\frac{\epsilon_0}{2} E^2$, while the contribution of the hydrogen atoms is $n \frac{1}{2} \alpha E^2$, where n is the number density. The total is then $\frac{1}{2} E^2 (\epsilon_0 + n\alpha) = \frac{1}{2} E^2 \epsilon_0 (1 + 4\pi \frac{9}{2} a_0{}^3 n)$. Therefore the permittivity of free space is changed to that of the gas, $\epsilon = \epsilon_0 (1 + 4\pi \frac{9}{2} a_0{}^3 n)$. At 0°C, 1atm, the number density is $n = \frac{N}{V} = \frac{p}{kT} = \frac{101.3\,\text{kPa}}{1.381\ 10^{-23}\ \text{JK}^{-1}\ 273.15\,K} = 2.69\ 10^{25}\ m^{-3}$, while $a_0 = 0.529\ 10^{-10}\ m$. Therefore, $\epsilon = \epsilon_0 * (1+0.000450)$.

The magnetic permeability also changes, but this correction is smaller by another factor of α^2 using the calculation in the previous problem:

$$\frac{1}{\mu_0} + n a^2 \frac{e^2}{4m} = \frac{1}{\mu_0} + n a^2 a \frac{m e^2}{4\pi\epsilon_0 \hbar^2} \frac{e^2}{4m} = \frac{1}{\mu_0} + n a^3 \frac{e^4}{16\pi\epsilon_0 \hbar^2}$$

$$= \frac{1}{\mu_0}\left(1 + n a^3 \frac{e^4 \mu_0}{16\pi\epsilon_0 \hbar^2}\right) = \frac{1}{\mu_0}\left(1 + n a^3 \frac{e^4}{16\pi\epsilon_0{}^2 \hbar^2 c^2}\right) = \frac{1}{\mu_0}(1 + n a^3 \pi \alpha^2)$$

Therefore we ignore this correction.

The speed of light is given by $c^2 / n^2 = 1/(\epsilon\mu)$, and hence in our case $n = \sqrt{\epsilon/\epsilon_0} = 1.000225$.

The measurement shows $n = 1.000140$ at $\lambda = 590$ mm. The correction to the index of refraction is obtained with the correct order of magnitude, while not right on. There are two reasons. One is that we dealt with hydrogen atom, not molecule. The second is that our calculation is for the spatially constant electric field, i.e. $\lambda = \infty$.

$$\frac{101.3 * 1000}{1.381\ 10^{-23} * 273.15}$$

2.68543×10^{25}

$$\% * (0.529\ 10^{-10})^3 * 4\pi * \frac{9}{2}$$

0.000224804

$\% * 2$

0.000449608