PHY 304, II-Semester 2023/24, Assignment 3 solution

(1) Integrations in atomic physics: [**8 pts**] In the week 3 and 4 material, you will see a few high dimensional integrations that frequently arise in atomic and molecular physics.[1] Feel free to provide a solution that is a hybrid between pen/paper and `mathematica`, but we need you to clearly discuss all steps that break down the original high dimensional integral into final 1D pieces.

(a) Find $\langle \frac{1}{r} \rangle$, $\langle \frac{1}{r^2} \rangle$ and $\langle \frac{1}{r^3} \rangle$ in a Hydrogen state $|\, n\ell m \,\rangle$ [Eq. (4.91)], used in section (7.3.1). *Solution: Mathematica can be used to directly compute the integrals if we explicitly specify some integers for n, ℓ, m. However it would be nice to know a general result, which it fails to provide. But we can manually find one as follows. The expectation value of r^k is given by*

$$\langle r^k \rangle = \int d^3\mathbf{r} \; r^k \psi^*_{nlm}(\mathbf{r})\psi_{nlm}(\mathbf{r}) \tag{1}$$

$$= \int_0^\infty dr \; r^{k+2}|R_{nl}(r)|^2 \int d\Omega \; |Y_{lm}(\theta,\varphi)|^2 \tag{2}$$

$$= \int_0^\infty dr \; N_{nl}^2 \; r^{k+2} e^{-\rho} \rho^{2l} \; (L_{n+l}^{2l+1}(\rho))^2 \tag{3}$$

*where we have used Eq. (7.133a) and (7.139a) from “**Bransden and Joachain, Quantum Mechanics**”*

$$\rho = \frac{2Z}{na} r \tag{4}$$

$$N_{nl} = -\left\{ \left(\frac{2Z}{na}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3} \right\}^{1/2} \tag{5}$$

Using Eq. (4) in Eq. (3) we get

$$\langle r^k \rangle = N_{nl}^2 \left(\frac{na}{2Z}\right)^{k+3} \int_0^\infty d\rho \; \rho^{2l+k+2} e^{-\rho} \; (L_{n+l}^{2l+1}(\rho))^2 \tag{6}$$

*To compute this integral we will make use of the generating function of associated Laguerre polynomials from Eq. (7.130) of “**Bransden and Joachain, Quantum Mechanics**”*

$$U_p(s,\rho) = \frac{(-s)^p}{(1-s)^{p+1}} \; \exp(-\rho s/(1-s)) \tag{7}$$

$$= \sum_{q=p}^{\infty} \frac{L_q^p(\rho)}{q!} s^q \tag{8}$$

Eq. (6), Eq. (7) and Eq. (8) as you shall see will be enough to calculate $\langle r^k \rangle$.

[1] There will be no problem to do this question prior to having gone through the week 4 material.

We start by realizing that due to Eq. (8),the product of generating functions $U_p(s,\rho)U_p(t,\rho)$ can yield terms of the form $L_q^p(\rho)^2$ and hence by first calculating the integral over this product, which can be easily evaluated due to Eq. (7), we can also extract our required integral over $L_{n+l}^{2l+1}(\rho)^2$ for suitable indices p and q.

We therefore begin with the following integral:

$$I = \int_0^\infty d\rho \; e^{-\rho}\rho^{2l+k+2}U_p(s,\rho)U_p(t,\rho) \tag{9}$$

We first use Eq. (7) to compute it explicitly:

$$I = \int_0^\infty d\rho \; \rho^{2l+k+2} \; \exp\left\{-\rho\left(1+\frac{s}{1-s}+\frac{t}{1-t}\right)\right\}\frac{(-s)^p(-t)^p}{(1-s)^{p+1}(1-t)^{p+1}} \tag{10}$$

Taking $u = \rho\left(1+\frac{s}{1-s}+\frac{t}{1-t}\right)$ *and the standard integral result*

$$\int_0^\infty du \; e^{-u} \; u^n = n! \tag{11}$$

we get,

$$I = \frac{(-s)^p(-t)^p}{(1-s)^{p+1}(1-t)^{p+1}}\left(1+\frac{s}{1-s}+\frac{t}{1-t}\right)^{-2l-k-3}\int_0^\infty du \; e^{-u} \; u^{2l+k+2} \tag{12}$$

$$= (-s)^p(-t)^p(1-st)^{-2l-k-3}(1-s)^{2l+k-p+2}(1-t)^{2l+k-p+2}(2l+k+2)! \tag{13}$$

We now use Eq. (8) to write Eq. (9) now also in terms of Associated Laguerre polynomials:

$$I = \sum_{i,j=p}^{\infty}\int_0^\infty d\rho \; e^{-\rho}\rho^{2l+k+2}L_i^p(\rho)L_j^p(\rho)\frac{s^i}{i!}\frac{t^j}{j!} \tag{14}$$

To compute the integral in Eq. (6) we need to equate the RHS of Eq. (13) with the RHS of Eq. (14)

I *Let us do this specifically for* $\langle 1/r\rangle$, *i.e. for* $k=-1$.

$$\sum_{i,j=p}^{\infty}\int_0^\infty d\rho \; e^{-\rho}\rho^{2l+1}L_i^p(\rho)L_j^p(\rho)\frac{s^i}{i!}\frac{t^j}{j!} = (-s)^{2l+1}(-t)^{2l+1}(1-st)^{-2l-2}(2l+1)! \tag{15}$$

$$= (2l+1)!\sum_{a=0}^{\infty}(-s)^{2l+1+a}(-t)^{2l+1+a}\binom{2l+a+1}{a} \tag{16}$$

where we used $(1-x)^{-n} = \sum_{a=0}^{\infty} \binom{n+a-1}{a} x^a$*. We now put* $p = 2l+1$ *and compare the LHS and RHS of Eq. (16) term by term to find that for* $i = j = n+l$ *in the LHS, the term with* $a = n-l-1$ *is picked up from the sum in the RHS (as coefficients of same power of* s *and* t*).*

We thus retrieve the integral we intended to find initially,

$$\int_0^{\infty} d\rho \; e^{-\rho} \rho^{2l+1} \frac{(L_{n+l}^{2l+1}(\rho))^2}{[(n+l)!]^2} = \frac{(n+l)!}{(2l+1)!(n-l-1)!} \times (2l+1)! \tag{17}$$

$$\implies \int_0^{\infty} d\rho \; e^{-\rho} \rho^{2l+1} (L_{n+l}^{2l+1}(\rho))^2 = \frac{((n+l)!)^3}{(n-l-1)!} \tag{18}$$

Using Eq. (18) and (5) in (6) we finally find

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{an^2} \tag{19}$$

II *Let us follow the same procedure for* $\langle 1/r^2 \rangle$ *i.e. for* $k = -2$*. Plugging this value of* k *in Eq. (13) and with* $p = 2l+1$*, we have*

$$I = (-s)^{2l+1}(-t)^{2l+1}(1-s)^{-1}(1-t)^{-1}(1-st)^{-2l-1}(2l)! \tag{20}$$

For each of the terms $(1-s)^{-1}$, $(1-t)^{-1}$ and $(1-st)^{-2l-1}$ we use the expansion $(1-x)^{-n} = \sum_{a=0}^{\infty} \binom{n+a-1}{a} x^a$ as before to re-write Eq. (20),

$$I = (2l)! \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} (-s)^{2l+1+a+c} (-t)^{2l+1+a+b} \binom{2l+a}{a} \tag{21}$$

In order to get co-efficients of $s^{n+l}t^{n+l}$ *from the above sum, we need* $a+b = n-l-1$ *and* $a+c = n-l-1$*.*

In order to identify these coefficients let us just look at,

$$\sum_{a=0}^{\infty} \sum_{c=0}^{\infty} (-s)^{2l+1+a+c}$$

We see that when $c = 0, 1 ... n-l-1$, we need "a" to be $n-l-1, n-l-2 ... 0$ in order to keep the exponent of s fixed to $n-l-1$. This then means that due to different c values we have terms of different "a" in the range $0, ..., n-l-1$ getting added.

Therefore the coefficient of the term $s^{n+l}t^{n+l}$ is:

$$(2l)! \sum_{a=0}^{n-l-1} \binom{2l+a}{a} = (2l)! \binom{n+l}{n-l-1} = \frac{(n+l)!}{(2l+1)(n-l-1)!} \tag{22}$$

where we have used the "hockey-stick identity" for the RHS

$$\sum_{r=0}^{m} \binom{n+r}{r} = \binom{n+m+1}{m} \tag{23}$$

whose proof is given in the appendix (You can easily find this on Wikipedia also) Therefore the integral in Eq. (14) for $k=-2$ is equal to the coefficient of $s^{n+l}t^{n+l}$ which we found in Eq. (22),

$$\int_0^\infty d\rho\; e^{-\rho}\rho^{2l}\frac{(L_{n+l}^{2l+1}(\rho))^2}{[(n+l)!]^2} = \frac{(n+l)!}{(2l+1)(n-l-1)!} \tag{24}$$

$$\implies \int_0^\infty d\rho\; e^{-\rho}\rho^{2l}(L_{n+l}^{2l+1}(\rho))^2 = \frac{((n+l)!)^3}{(2l+1)(n-l-1)!} \tag{25}$$

Using Eq. (25) and (5) in (6) we get

$$\left\langle \frac{1}{r^2}\right\rangle = \frac{2Z^2}{a^2n^3(2l+1)} \tag{26}$$

III *For $\langle 1/r^3\rangle$ we have $k=-3$. Following the same steps as before, Eq. (14) reads*

$$\begin{aligned} I &= (-s)^{2l+1}(-t)^{2l+1}(1-s)^{-2}(1-t)^{-2}(1-st)^{-2l}(2l-1)! \\ &= (2l-1)!\sum_{a=0}^{\infty}\sum_{b=0}^{\infty}\sum_{c=0}^{\infty}(-s)^{2l+1+a+c}(-t)^{2l+1+a+b}\binom{2l+a-1}{a}\binom{1+b}{b}\binom{1+c}{c} \\ &= (2l-1)!\sum_{a=0}^{\infty}\sum_{b=0}^{\infty}\sum_{c=0}^{\infty}(-s)^{2l+1+a+c}(-t)^{2l+1+a+b}(b+1)(c+1)\binom{2l+a-1}{a} \end{aligned} \tag{27}$$

where to reach Eq. (27) we have already used the binomial expansions for $(1-s)^{-2}, (1-t)^{-2}, (1-st)^{-2l}$ and explicitly calculated $\binom{1+b}{b}$ and $\binom{1+c}{c}$.

In order to identify the right coefficients we need $a+b+c=n-l-1$. We use the same logic used to find Eq. (22) and see that the coefficient of $s^{n+l}t^{n+l}$ from the sum turns out to be,

$$\begin{aligned} (2l-1)!\sum_{a=0}^{n-l-1}(n-l-1-a)^2\binom{2l+a-1}{a} &= (2l-1)!\frac{2n(n+l)!}{(n-l-1)!(2l+2)!} \\ &= \frac{n(n+l)!}{4(n-l-1)!\; l(l+\frac{1}{2})(l+1)} \end{aligned} \tag{28}$$

where we used the identity,

$$\sum_{a=0}^{k-1}(k-a)^2\binom{j+a}{a} = \frac{(j+2k+1)(j+k+1)!}{(k-1)!(j+3)!} \tag{29}$$

which is Eq. (144) derived in the appendix.

Comparing this coefficient with Eq. (14), we finally have

$$\int_0^\infty d\rho\; e^{-\rho}\rho^{2l-1}\frac{(L_{n+l}^{2l+1}(\rho))^2}{[(n+l)!]^2} = \frac{n(n+l)!}{4(n-l-1)!\; l(l+\frac{1}{2})(l+1)} \tag{30}$$

$$\Longrightarrow \int_0^\infty d\rho\; e^{-\rho}\rho^{2l-1}(L_{n+l}^{2l+1}(\rho))^2 = \frac{n[(n+l)!]^3}{4(n-l-1)!\; l(l+\frac{1}{2})(l+1)} \tag{31}$$

Using Eq. (31) and (5) in (6) we get

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a^3 n^3\; l(l+1)(l+\frac{1}{2})} \tag{32}$$

Note: *Another way to calculate these would be using the Feynman Hellman Theorem*

(b) Evaluate the overlapp integral $I = \int d^3\mathbf{r}\; \phi_{100}(\mathbf{r})\phi_{100}(\mathbf{r}')$ in Eq. (7.110), where ϕ_{100} is the Hydrogen ground-state wavefunction.
Solution: Using the hydrogen ground state wavefunction

$$\phi_{100}(\mathbf{r}') = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0} \tag{33}$$

the overlap integral Eq. (7.110) reads

$$I = \int d^3\mathbf{r}\phi_{100}(\mathbf{r})\phi_{100}(\mathbf{r}') \tag{34}$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi\; \frac{1}{\pi a_0^3} \sin\theta r^2 e^{-(r+r')/a_0} \tag{35}$$

Fig. (1) shows the vector $\mathbf{r}'$ *and how it is related to the vector* $\mathbf{r}$. *Using this in the equation above we get*

$$I = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi\; \frac{1}{\pi a_0^3} \sin\theta r^2 e^{-r/a_0} e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a_0} \tag{36}$$

Using the substitution $y = \sqrt{r^2+R^2-2rR\cos\theta}/a_0$ which gives $dy = \frac{1}{2ya_0^2}2rR\sin\theta d\theta$ we get

$$I = \frac{2}{a_0^3}\int_0^\infty drr^2 e^{-r/a_0} \int_{\sqrt{r^2+R^2-2rR}/a_0}^{\sqrt{r^2+R^2+2rR}/a_0} dy\; e^{-y}\frac{ya_0^2}{rR} \tag{37}$$

$$= \frac{2}{Ra_0}\int_0^\infty drr\; e^{-r/a_0}[-(y+1)e^{-y}]_{\sqrt{r^2+R^2-2rR}/a_0}^{\sqrt{r^2+R^2+2rR}/a_0} \tag{38}$$

$$= \frac{2}{Ra_0}\int_0^\infty drr\; e^{-r/a_0}\left\{-\left(\frac{r+R}{a_0}+1\right))e^{-(r+R)/a_0} + \left(\frac{|r-R|}{a_0}+1\right)e^{-|r-R|/a_0}\right\} \tag{39}$$

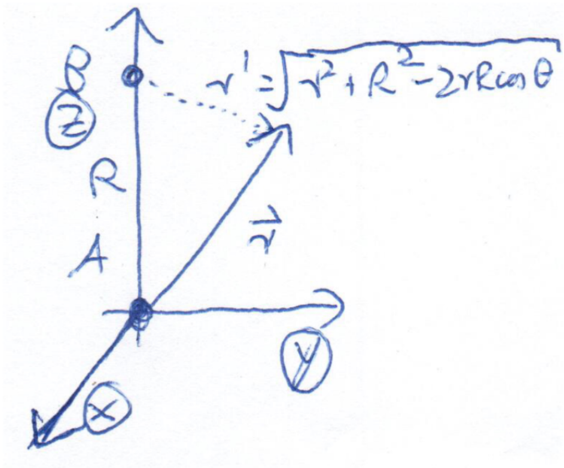

Figure 1: Refer to this coordinate diagram to see how we replaced r' by its dependence on r. For this we used $\mathbf{r'}^2 = (\mathbf{r} - \mathbf{R})^2 = \mathbf{r}^2 + \mathbf{R}^2 - 2\mathbf{r} \cdot \mathbf{R} = r^2 + R^2 - 2rRcos\theta$

We need to split the above integral in two parts:

$$\int_0^\infty dr f(r) = \int_0^R dr f(r < R) + \int_R^\infty f(r > R) \tag{40}$$

This gives us

$$I = \frac{2}{Ra_0}\left(\int_0^R dr \left\{\left(\frac{r(R-r)}{a_0} + r\right) e^{-R/a_0} - \left(\frac{r(r+R)}{a_0} + r\right) e^{-2r/a_0} e^{-R/a_0}\right\}\right.$$
$$\left. + \int_R^\infty dr \left\{\left(\frac{r(r-R)}{a_0} + r\right) e^{-2r/a_0} e^{R/a_0} - \left(\frac{r(r+R)}{a_0} + r\right) e^{-2r/a_0} e^{-R/a_0}\right\}\right) \tag{41}$$
$$= \frac{2}{Ra_0}\left(\int_0^R dr \left\{\frac{rR}{a_0} - \frac{r^2}{a_0} + r - \frac{r^2}{a_0} e^{-2r/a_0} - \frac{rR}{a_0} e^{-2r/a_0} - re^{-2r/a_0}\right\} e^{-R/a_0}\right.$$
$$\left. + \int_R^\infty dr \left\{\left(\frac{r^2}{a_0} - \frac{rR}{a_0} + r\right) e^{R/a_0} - \left(\frac{r^2}{a_0} + \frac{rR}{a_0} + r\right) e^{-R/a_0}\right\} e^{-2r/a_0}\right) \tag{42}$$

Using the standard integral results

$$\int dx\ xe^{-x} = -(x+1)e^{-x} \tag{43}$$
$$\int dx\ x^2 e^{-x} = -(x^2 + 2x + 2)e^{-x} \tag{44}$$

We get

$$I = e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{1}{3}\frac{R^2}{a_0^2}\right) \tag{45}$$

(c) Evaluate the direct and exchange integrals in Eq. (7.113), Eq. (7.114).

$$I_{\rm dir} = a_0 \int d^3\mathbf{r}\, \phi_{100}(\mathbf{r}) \frac{1}{r'} \phi_{100}(\mathbf{r}) = \frac{a_0}{R} - \left(1 + \frac{a_0}{R}\right) e^{-2R/a_0}, \tag{46}$$

$$I_{\rm ex} = a_0 \int d^3\mathbf{r}\, \phi_{100}(\mathbf{r}) \frac{1}{r} \phi_{100}(\mathbf{r}') = \left(1 + \frac{a_0}{R}\right) e^{-R/a_0}. \tag{47}$$

Solution: Following the same steps as in part(b) the direct integral reads

$$I_{dir} = a_0 \int_0^\infty dr\ r^2 \frac{1}{\pi a_0^3} e^{-2r/a_0} \int_0^\pi d\theta\ \sin\theta \frac{1}{\sqrt{r^2 + R^2 - 2rR\cos\theta}} \int_0^{2\pi} d\varphi \tag{48}$$

Substituing $y = \sqrt{r^2 + R^2 - 2rR\cos\theta}$ *which gives* $dy = \frac{rR}{y}\sin\theta d\theta$, *we get*

$$\begin{aligned}
I_{dir} &= \frac{2}{Ra_0^2} \int_0^\infty dr\ re^{-2r/a_0} \int_{\sqrt{r^2+R^2-2rR}}^{\sqrt{r^2+R^2+2rR}} dy & (49)\\
&= \frac{2}{Ra_0^2} \int_0^\infty dr\ re^{-2r/a_0} \{(r+R) - |r-R|\} & (50)\\
&= \frac{2}{Ra_0^2} \left(\int_0^R dr\ 2r^2 e^{-2r/a_0} + \int_R^\infty dr\ 2rRe^{-2r/a_0} \right) & (51)\\
&= \frac{4}{Ra_0^2} \left(\frac{a_0^3}{4} - \frac{e^{-2R/a_0}}{4}(a_0^3 + 2Ra_0^2 + 2R^2 a_0) + \frac{e^{-2R/a_0}}{4}(Ra_0^2 + 2R^2 a_0) \right) & (52)\\
&= \frac{a_0}{R} - \left(1 + \frac{a_0}{R}\right) e^{-2R/a_0} & (53)
\end{aligned}$$

The exchange integral reads

$$I_{ex} = a_0 \int_0^\infty dr\ r^2 \frac{1}{\pi a_0^3} e^{-r/a_0} \frac{1}{r} \int_0^\pi d\theta\ \sin\theta e^{-\sqrt{r^2+R^2-2rR\cos\theta}/a_0} \int_0^{2\pi} d\varphi \tag{54}$$

Substituting $y = \sqrt{r^2 + R^2 - 2rR\cos\theta}/a_0$ *which gives* $dy = \frac{1}{2ya_0^2} 2rR\sin\theta d\theta$, *we get*

$$\begin{aligned}
I_{ex} &= \frac{2}{R} \int_0^\infty e^{-r/a_0} \int_{\sqrt{r^2+R^2-2rR}/a_0}^{\sqrt{r^2+R^2+2rR}/a_0} dy\ ye^{-y} & (55)\\
&= \frac{2}{R} \int_0^\infty dre^{-r/a_0} \left\{ \left(\frac{|r-R|}{a_0} + 1\right) e^{-|r-R|/a_0} - \left(\frac{r+R}{a_0} + 1\right) e^{-(r+R)/a_0} \right\} & (56)\\
&= \frac{2}{R} \Bigg(\int_0^\infty dr \left(-\frac{r}{a_0} - \frac{R}{a_0} - 1\right) e^{-2r/a_0} e^{-R/a_0} + \int_0^R dr \left(\frac{R-r}{a_0} + 1\right) e^{-R/a_0} \\
&\qquad + \int_R^\infty dr \left(\frac{r-R}{a_0} + 1\right) e^{-2r/a_0} e^{R/a_0} \Bigg) & (57)\\
&= \frac{2}{R} \left(\frac{R}{2} e^{-R/a_0} + \frac{R^2}{2a_0} e^{-R/a_0} \right) = \left(1 + \frac{R}{a_0}\right) e^{-R/a_0} & (58)
\end{aligned}$$

(2) Potential well with linear slope: [6 pts] A particle of mass m is trapped in a potential well of the form $V(x) = \beta|x|$ with $\beta > 0$.

(a) Sketch this potential and the expected shape and symmetries of the ground-state wavefunction and justify your answers.
Solution:
(a) For the potential $V(x) = \beta|x|$, shown below as orange line,

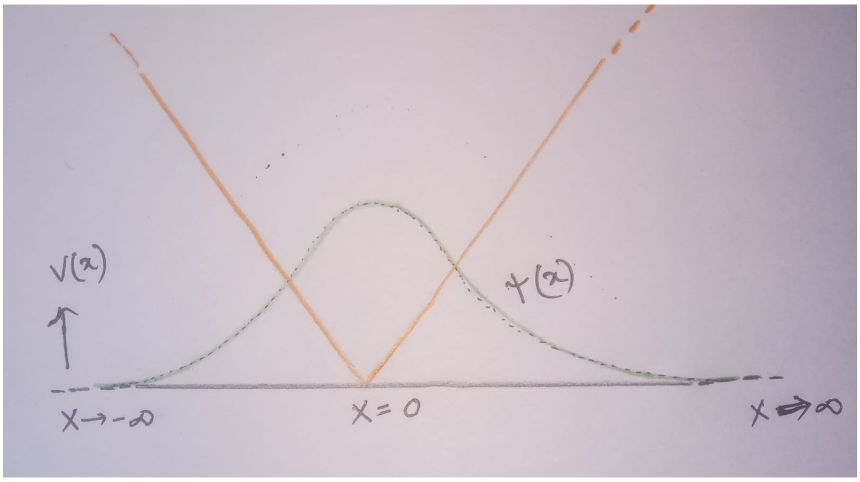

Figure 2: Sketch of potential $V(x) = \beta|x|$ (orange) and rough expectation of the ground-state wavefunction (black).

we expect the following basic features for the ground-state wavefunction:

(a) Ground state wave function should be symmetric around $x = 0$.

(b) It cannot have any nodes.

(c) In the classically forbidden region, it should decay exponentially.

(b) In order to find the ground-state, decide on your own trial wavefunction for the variational method with at least one variational parameter and justify your choices.
Solution: A trial function that fulfills all the above criteria is

$$\psi(x) = \mathcal{N} e^{-\frac{x^2}{2\sigma^2}}. \tag{59}$$

We could also take other functions that fulfill them. In Eq. (59), $\mathcal{N}$ is the normalization factor with $\mathcal{N} = \frac{1}{\sqrt{\sigma}\pi^{1/4}}$ and the width σ is taken as variational parameter. The reason for choosing this wavefunction is, that it is symmetric about $x = 0$, has no nodes, and decays in the classically forbidden region.

(c) Using that trial wavefunction, find an approximation to the ground-state wavefunction and energy.

Solution: In order to calculate the ground state wavefunction, we begin by calculating the energy expectation value:

$$\langle \psi \,|\, H|\psi \,\rangle = \frac{1}{\sigma\pi^{1/2}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \beta|x| \right) e^{-\frac{x^2}{2\sigma^2}} \, dx \tag{60}$$

$$= \frac{1}{\sigma\pi^{1/2}} \left(\int_{-\infty}^{0} \left(\frac{\hbar^2}{2m\sigma^2} - \frac{\hbar^2 x^2}{2m\sigma^4} - \beta x \right) e^{-\frac{x^2}{\sigma^2}} \, dx + \int_{0}^{\infty} \left(\frac{\hbar^2}{2m\sigma^2} - \frac{\hbar^2 x^2}{2m\sigma^4} + \beta x \right) e^{-\frac{x^2}{\sigma^2}} \, dx \right) \tag{61}$$

$$= \frac{2}{\sigma\pi^{1/2}} \left(\int_{0}^{\infty} \left(\frac{\hbar^2}{2m\sigma^2} - \frac{\hbar^2 x^2}{2m\sigma^4} + \beta x \right) e^{-\frac{x^2}{\sigma^2}} \, dx \right) \tag{62}$$

Using,

$$\int_0^\infty x e^{-\frac{x^2}{\sigma^2}} \, dx = \frac{\sigma^2}{2} \tag{63}$$

$$\int_0^\infty e^{-\frac{x^2}{\sigma^2}} \, dx = \frac{\sigma\sqrt{\pi}}{2} \tag{64}$$

$$\int_0^\infty x^2 e^{-\frac{x^2}{\sigma^2}} \, dx = \frac{\sigma^3\sqrt{\pi}}{4}, \tag{65}$$

this integral can be evaluated to give:

$$E(\sigma) = \langle \psi \,|\, H|\psi \,\rangle = \frac{\beta\sigma}{\sqrt{\pi}} + \frac{\hbar^2}{4m\sigma^2} \tag{66}$$

We now minimize $E(\sigma)$:

$$\frac{dE(\sigma)}{d\sigma} = \frac{\beta}{\sqrt{\pi}} - \frac{\hbar^2}{2m\sigma^3} = 0 \tag{67}$$

to get

$$\sigma = \left(\frac{\hbar^2 \sqrt{\pi}}{2m\beta} \right)^{1/3}. \tag{68}$$

(d) The exact solution[2] of this problem has a ground-state energy

$$E_g = 1.01879 \left(\frac{\beta^2 \hbar^2}{2m} \right)^{1/3} \tag{69}$$

and wavefunction

$$\phi_g(x) = 1.21954 \left(\frac{2m\beta}{\hbar^2} \right)^{1/6} \times Ai \left(\left(\frac{2m\beta}{\hbar^2} \right)^{1/3} |x| - 1.01879 \right) \tag{70}$$

[2]Please do not use this kind of function as trial function in (b).

Compare your solution for the energy with Eq. (69) and discuss why/how the variational method has helped. Similarly, compare your trial solution with the true solution in the same figure using e.g. `mathematica` for several different parameters, and discuss your achievements.

Solution:

Inserting the value of σ (from Eq. (68)) to find the energy in Eq. (66) calculated from the trial wavefunction, we get

$$E = 1.0241 \left(\frac{\beta^2 \hbar^2}{2m} \right)^{1/3} . \tag{71}$$

This energy value for the ground state is a good approximation of the exact energy value mentioned in the question, in particular it captures all the power laws through which the energy depends on the parameters of the problem (β, m) correctly.

We can also compare the trial wavefunction Eq. (59) with σ taken from Eq. (68) with the exact ground state wavefunction Eq. (70), as shown in Fig. 3. We can see that the trial wavefunction gets very close, and we see from the expressions for the wavefunction widths that it also captures all the essential dependencies on parameters for that.

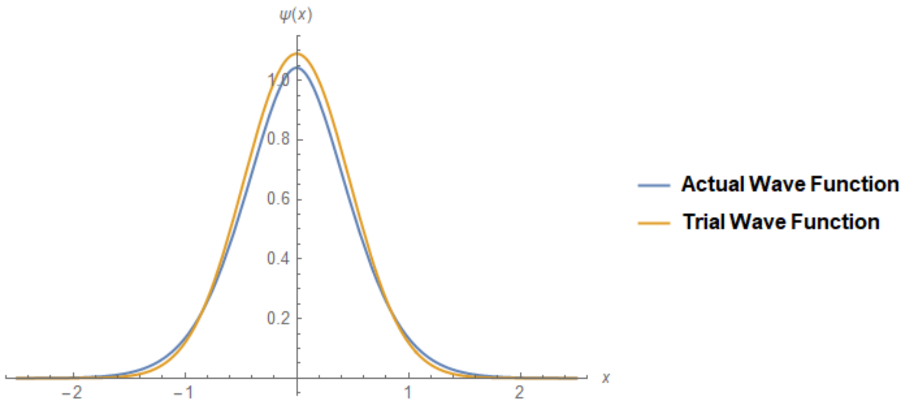

Figure 3: Comparison of the optimised trial wavefunction Eq. (59) (orange) with the true ground-state of the triangular well Eq. (70) (blue).

(3) Higher order perturbation theory: [8 pts] Following our approach of "week 2", derive the third order correction of the energy $\lambda^3 E_n^{(3)}$ and the second order correction to the quantum states $\lambda^2 |\, \psi_n^{(2)} \,\rangle$.

Solution: Following the same arguments as given in section (7.1) of the lecture notes, we can write the power series of both $|\, \psi_n \,\rangle$ and E_n as:

$$|\, \psi_n \,\rangle = |\, \psi_n^{(0)} \,\rangle + \lambda |\, \psi_n^{(1)} \,\rangle + \lambda^2 |\, \psi_n^{(2)} \,\rangle + ... = \sum_{k=0}^{\infty} \lambda^k |\, \psi_n^{(k)} \,\rangle \tag{72}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} ... = \sum_{k=0}^{\infty} \lambda^k E_n^{(k)} \tag{73}$$

Inserting Eq. (72) and Eq. (73) into the eigenvalue problem

$$\hat{H} |\, \psi_n \,\rangle = E_n |\, \psi_n \,\rangle \tag{74}$$

we get:

$$\begin{aligned} \left(\hat{H}^{(0)} + \lambda \hat{H}^{'}\right) \left(|\, \psi_n^{(0)} \,\rangle + \lambda |\, \psi_n^{(1)} \,\rangle + \lambda^2 |\, \psi_n^{(2)} \,\rangle + ...\right) = \\ \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} ...\right) \left(|\, \psi_n^{(0)} \,\rangle + \lambda |\, \psi_n^{(1)} \,\rangle + \lambda^2 |\, \psi_n^{(2)} \,\rangle + ...\right) \end{aligned} \tag{75}$$

Using the fact that different powers of λ are linearly independent,

$$for\ \lambda : \quad \hat{H}^{(0)} |\, \psi_n^{(1)} \,\rangle + \hat{H}^{'} |\, \psi_n^{(0)} \,\rangle = E_n^{(0)} |\, \psi_n^{(1)} \,\rangle + E_n^{(1)} |\, \psi_n^{(0)} \,\rangle, \tag{76}$$

$$for\ \lambda^2 : \quad \hat{H}^{(0)} |\, \psi_n^{(2)} \,\rangle + \hat{H}^{'} |\, \psi_n^{(1)} \,\rangle = E_n^{(0)} |\, \psi_n^{(2)} \,\rangle + E_n^{(1)} |\, \psi_n^{(1)} \,\rangle + E_n^{(2)} |\, \psi_n^{(0)} \,\rangle, \tag{77}$$

$$for\ \lambda^3 : \hat{H}^{(0)} |\, \psi_n^{(3)} \,\rangle + \hat{H}^{'} |\, \psi_n^{(2)} \,\rangle = E_n^{(0)} |\, \psi_n^{(3)} \,\rangle + E_n^{(1)} |\, \psi_n^{(2)} \,\rangle + E_n^{(2)} |\, \psi_n^{(1)} \,\rangle + E_n^{(3)} |\, \psi_n^{(0)} \,\rangle, \tag{78}$$

Multiplying Eq. (78) with $\langle\, \psi_n^{(0)} \,|$ we get,

$$\underbrace{\langle\, \psi_n^{(0)} \,|\, \hat{H}^{(0)} | \psi_n^{(3)} \,\rangle}_{= E_n^{(0)} \langle\, \psi_n^{(0)} \,|\, \psi_n^{(3)} \,\rangle} + \langle\, \psi_n^{(0)} \,|\, \hat{H}' | \psi_n^{(2)} \,\rangle = E_n^{(0)} \langle\, \psi_n^{(0)} \,|\, \psi_n^{(3)} \,\rangle + E_n^{(1)} \underbrace{\langle\, \psi_n^{(0)} \,|\, \psi_n^{(2)} \,\rangle}_{=0} + E_n^{(2)} \underbrace{\langle\, \psi_n^{(0)} \,|\, \psi_n^{(1)} \,\rangle}_{=0} + E_n^{(3)}, \tag{79}$$

where we have used $\langle\, \psi_n^{(0)} \,|\, \psi_n^{(1,2)} \,\rangle = 0$ (in order to preserve normalisation of the perturbed state, see Griffith).

We then get,

$$E_n^{(3)} = \langle\, \psi_n^{(0)} \,|\, \hat{H}^{'} | \psi_n^{(2)} \,\rangle \tag{80}$$

Using Eq. (77) and re-arranging, we get:

$$\hat{H}^{(0)} |\, \psi_n^{(2)} \,\rangle - E_n^{(0)} |\, \psi_n^{(2)} \,\rangle = E_n^{(1)} |\, \psi_n^{(1)} \,\rangle + E_n^{(2)} |\, \psi_n^{(0)} \,\rangle - \hat{H}^{'} |\, \psi_n^{(1)} \,\rangle \tag{81}$$

Now we recognise that we can express

$$|\, \psi_n^{(2)} \,\rangle = \sum_{m \neq n} c_m^{(n)} |\, \psi_m^{(0} \,\rangle \tag{82}$$

since the $|\,\psi_m^{(0}\,\rangle$ *form a basis of the Hilbertspace (and we do not add* $|\,\psi_m^{(0}\,\rangle$*, to preserve normalisation of the perturbed state), and insert Eq. (82) into:*

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)|\,\psi_n^{(2)}\,\rangle = \left(E_n^{(1)} - \hat{H}'\right)|\,\psi_n^{(1)}\,\rangle + E_n^{(2)}|\,\psi_n^{(0)}\,\rangle, \tag{83}$$

to reach:

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)\sum_{m\neq n} c_m^{(n)}|\,\psi_m^{(0}\,\rangle = \left(E_n^{(1)} - \hat{H}'\right)|\,\psi_n^{(1)}\,\rangle + E_n^{(2)}|\,\psi_n^{(0)}\,\rangle \tag{84}$$

On the LHS we use that $H^{(0)}|\,\psi_m^{(0}\,\rangle = E_m^{(0)}|\,\psi_m^{(0}\,\rangle$ *and on the RHS we insert the expression for the first order correction of eigenstates* $|\,\psi_n^{(1)}\,\rangle$ *that we found earlier:*

$$\sum_{m\neq n} c_m^{(n)}\left(E_m^{(0)} - E_n^{(0)}\right)|\,\psi_m^{(0}\,\rangle = \left(E_n^{(1)} - \hat{H}'\right)\sum_{l\neq n}\frac{\langle\,\psi_l^{(0)}\,|\,\hat{H}'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}}|\,\psi_l^{(0)}\,\rangle + E_n^{(2)}|\,\psi_n^{(0)}\,\rangle \tag{85}$$

Now multiplying Eq. (85) with $\langle\,\psi_j^{(0)}\,|$*, using* $\langle\,\psi_j^{(0)}\,|\,\psi_m^{(0)}\,\rangle = \delta_{j,m}$ *and only taking the case for* $j \neq n$ *(since for* $j = n$ *we recover the 2nd order perturbation correction) we get,*

$$c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right) = E_n^{(1)}\sum_{l\neq n}\frac{\langle\,\psi_l^{(0)}\,|\,\hat{H}'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}}\underbrace{\langle\,\psi_j^{(0)}\,|\,\psi_l^{(0)}\,\rangle}_{=\delta_{l,j}} - \sum_{l\neq n}\frac{\langle\,\psi_l^{(0)}\,|\,\hat{H}'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}}\langle\,\psi_j^{(0)}|\hat{H}'\,|\,\psi_l^{(0)}\,\rangle \tag{86}$$

which gives the co-efficients as:

$$c_j^{(n)} = \sum_{l\neq n}\frac{\langle\,\psi_j^{(0)}|\hat{H}'\,|\,\psi_l^{(0)}\,\rangle}{E_j^{(0)} - E_n^{(0)}}\frac{\langle\,\psi_l^{(0)}\,|\,\hat{H}'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}} - E_n^{(1)}\frac{\langle\,\psi_j^{(0)}|\hat{H}'\,|\,\psi_n^{(0)}\,\rangle}{(E_n^{(0)} - E_j^{(0)})^2} \tag{87}$$

By using Eq. (87) (with $c_j^{(n)}$ *replaced by* $c_m^{(n)}$*) in Eq. (82) we finally get the 2nd order state correction:*

$$|\,\psi_n^{(2)}\,\rangle = \sum_{m\neq n}\sum_{l\neq n}\frac{\langle\,\psi_m^{(0)}\,|\,H'|\psi_l^{(0)}\,\rangle}{E_m^{(0)} - E_n^{(0)}}\frac{\langle\,\psi_l^{(0)}\,|\,H'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}}|\,\psi_m^{(0)}\,\rangle - \sum_{m\neq n} E_n^{(1)}\frac{\langle\,\psi_m^{(0)}|\hat{H}'\,|\,\psi_n^{(0)}\,\rangle}{(E_n^{(0)} - E_m^{(0)})^2}|\,\psi_m^{(0)}\,\rangle \tag{88}$$

Now using Eq. (88) into Eq. (80) we also finally get the third order energy correction:

$$E_n^{(3)} = \sum_{m\neq n}\sum_{l\neq n}\frac{\langle\,\psi_m^{(0)}\,|\,H'|\psi_l^{(0)}\,\rangle}{E_m^{(0)} - E_n^{(0)}}\frac{\langle\,\psi_l^{(0)}\,|\,H'|\psi_n^{(0)}\,\rangle}{E_n^{(0)} - E_l^{(0)}}\langle\,\psi_n^{(0)}\,|\,H'|\psi_m^{(0)}\,\rangle - \sum_{m\neq n}\frac{\langle\,\psi_n^{(0)}\,|\,H'|\psi_n^{(0)}\,\rangle|\langle\,\psi_m^{(0)}\,|\,H'|\psi_n^{(0)}\,\rangle|^2}{(E_n^{(0)} - E_m^{(0)})^2} \tag{89}$$

(4) Perturbation theory versus exact calculation: [**8 pts**] Consider the Hamiltonian in matrix form (basis $\{|\,1\,\rangle, |\,2\,\rangle, \cdots |\,6\,\rangle\}$)

$$\hat{H} = \begin{bmatrix} E_a & 0 & \kappa & 0 & 0 & 0 \\ 0 & E_a & 0 & 0 & -\kappa & 0 \\ \kappa & 0 & E_a & 0 & 0 & 0 \\ 0 & 0 & 0 & E_b & 0 & 2\kappa \\ 0 & -\kappa & 0 & 0 & E_b & 0 \\ 0 & 0 & 0 & 2\kappa & 0 & E_b \end{bmatrix}, \tag{90}$$

for real and positive E_a, E_b, κ, let $E_b > E_a$.

(a) Assuming $\kappa \ll E_a, E_b$, use the appropriate type of perturbation theory to find all perturbed eigenvalues and eigenvectors to order κ.

Solution:

For $\kappa \ll E_a, E_b$, the splitting becomes,

$$\hat{H} = \underbrace{\begin{bmatrix} E_a & 0 & 0 & 0 & 0 & 0 \\ 0 & E_a & 0 & 0 & 0 & 0 \\ 0 & 0 & E_a & 0 & 0 & 0 \\ 0 & 0 & 0 & E_b & 0 & 0 \\ 0 & 0 & 0 & 0 & E_b & 0 \\ 0 & 0 & 0 & 0 & 0 & E_b \end{bmatrix}}_{\hat{H}^{(0)}} + \underbrace{\begin{bmatrix} 0 & 0 & \kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\kappa & 0 \\ \kappa & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\kappa \\ 0 & -\kappa & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\kappa & 0 & 0 \end{bmatrix}}_{\hat{H}'}, \tag{91}$$

It is clear we have to use the *degenerate perturbation theory.*

For that we separately diagonalize (can be done by hand or using Mathematica) the subspaces:

$$\hat{H}_1 = \begin{bmatrix} 0 & 0 & \kappa \\ 0 & 0 & 0 \\ \kappa & 0 & 0 \end{bmatrix} \tag{92}$$

which gives the eigenvalues as: $\{-\kappa, \kappa, 0\}$ and coefficient eigenvectors that mix the unperturbed basis states as: $\{\{-1, 0, 1\}, \{1, 0, 1\}, \{0, 1, 0\}\}$

and

$$\hat{H}_2 = \begin{bmatrix} 0 & 0 & 2\kappa \\ 0 & 0 & 0 \\ 2\kappa & 0 & 0 \end{bmatrix} \tag{93}$$

which gives the eigenvalues as: $\{-2\kappa, 2\kappa, 0\}$ and coefficient eigenvectors that mix the unperturbed basis states as: $\{\{-1, 0, 1\}, \{1, 0, 1\}, \{0, 1, 0\}\}$

The perturbed eigenvalues and eigenvectors to order κ then finally are :

$$\lambda_1 = E_a - \kappa \ , \qquad |\,\psi_1\,\rangle = -1 \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + 1 \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \left[\ -1 \ \ 0 \ \ 1 \ \ 0 \ \ 0 \ \ 0\ \right]^{\mathbf{T}}; \tag{94}$$

$$\lambda_2 = E_a + \kappa \ , \qquad |\,\psi_2\,\rangle = 1 \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} + 1 \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \left[\ 1 \ \ 0 \ \ 1 \ \ 0 \ \ 0 \ \ 0\ \right]^{\mathbf{T}} \tag{95}$$

$$\lambda_3 = E_a + 0 \ , \qquad |\,\psi_3\,\rangle = \left[\ 0 \ \ 1 \ \ 0 \ \ 0 \ \ 0 \ \ 0\ \right]^{\mathbf{T}} \tag{96}$$

$$\lambda_4 = E_b - 2\kappa \ , \qquad |\,\psi_4\,\rangle = -1 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} + 1 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \left[\ 0 \ \ 0 \ \ 0 \ \ -1 \ \ 0 \ \ 1\ \right]^{\mathbf{T}} \tag{97}$$

$$\lambda_5 = E_b + 2\kappa \ , \qquad |\,\psi_5\,\rangle = 1 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} + 1 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}} \left[\ 0 \ \ 0 \ \ 0 \ \ 1 \ \ 0 \ \ 1\ \right]^{\mathbf{T}} \tag{98}$$

$$\lambda_6 = E_b + 0 \ , \qquad |\,\psi_6\,\rangle = \left[\ 0 \ \ 0 \ \ 0 \ \ 0 \ \ 1 \ \ 0\ \right]^{\mathbf{T}} \tag{99}$$

(b) Now going to the inverse limit of $\kappa \gg |E_b - E_a|$, use the appropriate type of perturbation theory to find all perturbed eigenvalues and eigenvectors to order $|E_b - E_a|$. *Hint: First simplify the Hamiltonian by re-adjusting the zero of energy. Then change into the eigenbasis appropriate for large κ.*

Solution: We start by re-adjusting the zero of energy to E_a after which, for $\kappa \gg |E_b - E_a|$, the splitting becomes:

$$\hat{H} = \underbrace{\begin{bmatrix} 0 & 0 & \kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\kappa & 0 \\ \kappa & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\kappa \\ 0 & -\kappa & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\kappa & 0 & 0 \end{bmatrix}}_{\hat{H}^{(0)}} + \underbrace{\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_b - E_a & 0 & 0 \\ 0 & 0 & 0 & 0 & E_b - E_a & 0 \\ 0 & 0 & 0 & 0 & 0 & E_b - E_a \end{bmatrix}}_{\hat{H}'}, \tag{100}$$

To look for degeneracies in $\hat{H}^{(0)}$ we first diagonalize it (using Mathematica) to get eigenvalues as: $\{-2\kappa, 2\kappa, -\kappa, -\kappa, \kappa, \kappa\}$ and co-efficient eigenvectors as: $\{\frac{1}{\sqrt{2}}\{0,0,0,-1,0,1\}, \frac{1}{\sqrt{2}}\{0,0,0,-1,0,-1\}, \frac{1}{\sqrt{2}}\{0,1,0,0,1,0\}, \frac{1}{\sqrt{2}}\{-1,0,1,0,0,0\}, \frac{1}{\sqrt{2}}\{0,-1,0,0,1$ $, \frac{1}{\sqrt{2}}\{1,0,1,0,0,0\}\}$.

We see that there indeed are degeneracies for which we need degenerate perturbation theory.

For a clearer analysis of the problem, we first change basis for both parts of the Hamiltonian to eigenstates of $H^{(0)}$.

We know that if $\{\mathbf{v}_1, \mathbf{v}_2, ..., \mathbf{v}_n\}$ are eigenvectors of a matrix then the transformation matrix that diagonalises it is $P = [\mathbf{v}_1\ \mathbf{v}_2\ \cdots\ \mathbf{v}_n]$. For our case,

$$P = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ -1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{101}$$

Therefore, $\hat{H}^{(0)}_{new} = P^{-1}\hat{H}^{(0)}P$ and $\hat{H}'_{new} = P^{-1}\hat{H}'P$ (note that P is orthogonal so that $P^{-1} = P^T$) such that both parts of the Hamiltonian now become:

$$\hat{H}^{(0)}_{new} = \begin{bmatrix} -2\kappa & 0 & 0 & 0 & 0 & 0 \\ 0 & 2\kappa & 0 & 0 & 0 & 0 \\ 0 & 0 & -\kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & -\kappa & 0 & 0 \\ 0 & 0 & 0 & 0 & \kappa & 0 \\ 0 & 0 & 0 & 0 & 0 & \kappa \end{bmatrix} \quad \hat{H}'_{new} = \begin{bmatrix} E_b - E_a & 0 & 0 & 0 & 0 & 0 \\ 0 & E_b - E_a & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{(E_b-E_a)}{2} & 0 & \frac{(E_b-E_a)}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{(E_b-E_a)}{2} & 0 & \frac{(E_b-E_a)}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{102}$$

For the two non-degenerate eignevalues (-2κ and 2κ) we use non-degenerate perturbation theory ($\langle\, \phi \,|\, H' |\phi\, \rangle$) to get $E_b - E_a$ as energy corrections for both.

The degenerate sub-spaces corresponding to both $-\kappa$ and κ turn out to be diagonal already.

The perturbed eigenvalues and eigenvectors then finally are:

$$\lambda_1 = -2\kappa + (E_b - E_a) \ , \qquad |\,\psi_1^{new}\,\rangle = \left[\begin{array}{cccccc} 1 & 0 & 0 & 0 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{103}$$

$$\lambda_2 = 2\kappa + (E_b - E_a) \ \ , \qquad |\,\psi_2^{new}\,\rangle = \left[\begin{array}{cccccc} 0 & 1 & 0 & 0 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{104}$$

$$\lambda_3 = -\kappa + \frac{(E_b - E_a)}{2} \ \ , \qquad |\,\psi_3^{new}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 1 & 0 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{105}$$

$$\lambda_4 = -\kappa + 0 \ \ , \qquad |\,\psi_4^{new}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 0 & 1 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{106}$$

$$\lambda_5 = \kappa + \frac{(E_b - E_a)}{2} \ \ , \qquad |\,\psi_5^{new}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 0 & 0 & 1 & 0 \end{array}\right]^{\mathbf{T}} \tag{107}$$

$$\lambda_6 = \kappa + 0 \ \ , \qquad |\,\psi_6^{new}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right]^{\mathbf{T}} \tag{108}$$

These eigenvectors though are in the transformed basis. To get back in the original basis we use $|\psi_n^{old} >= P|\psi_n^{new} >$ to finally get,

$$\lambda_1 = -2\kappa + (E_b - E_a) \ , \qquad |\,\psi_1^{old}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{array}\right]^{\mathbf{T}} \tag{109}$$

$$\lambda_2 = 2\kappa + (E_b - E_a) \ \ , \qquad |\,\psi_2^{old}\,\rangle = \left[\begin{array}{cccccc} 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{array}\right]^{\mathbf{T}} \tag{110}$$

$$\lambda_3 = -\kappa + \frac{(E_b - E_a)}{2} \ \ , \qquad |\,\psi_3^{old}\,\rangle = \left[\begin{array}{cccccc} 0 & \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \end{array}\right]^{\mathbf{T}} \tag{111}$$

$$\lambda_4 = -\kappa + 0 \ \ , \qquad |\,\psi_4^{old}\,\rangle = \left[\begin{array}{cccccc} -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{112}$$

$$\lambda_5 = \kappa + \frac{(E_b - E_a)}{2} \ \ , \qquad |\,\psi_5^{old}\,\rangle = \left[\begin{array}{cccccc} -\frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{113}$$

$$\lambda_6 = \kappa + 0 \ \ , \qquad |\,\psi_6^{old}\,\rangle = \left[\begin{array}{cccccc} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \end{array}\right]^{\mathbf{T}} \tag{114}$$

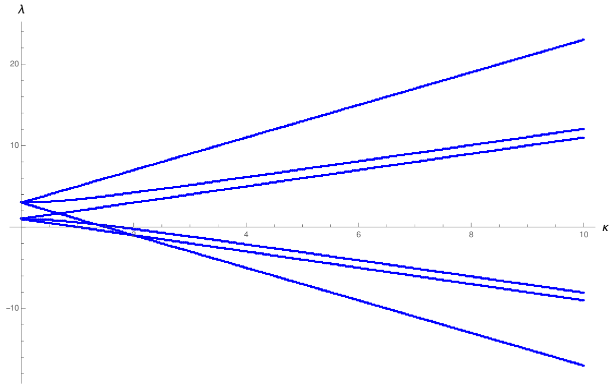

Figure 4: Displays degeneracy lifting as κ increases

(c) Finally, checkout the spectrum over the whole range of $0 < \kappa < 10$ adapting `Assignment3_program_draft_v2.nb` at the XXX in the code. Discuss your results. Also discuss the behavior of eigenvalues across the whole range of κ and check out how one interesting eigenvector changes with κ.

Solution: The Mathematica file `Assignment3_program_solution_v2.nb` plots the eigenvalues as a function of κ as:

To show how an interesting eigenvector (one that changes with κ) depends on κ we plot the 5th eigenvector below: We see that the eigenvector itself changes from $|\,\phi_5\,\rangle = |\,2\,\rangle$ at $\kappa = 0$ to $|\,\phi_5\,\rangle \approx (|\,2\,\rangle + |\,5\,\rangle)/\sqrt{2}$ at large κ.

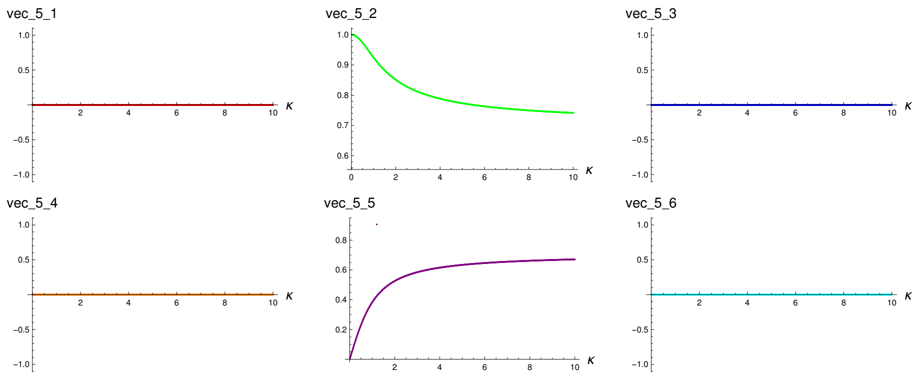

Figure 5: Here, "vec51" means the 1st component of the 5th eigenvector, i.e. $\langle\,1\,|\,\phi_5\,\rangle$ and so on.

(5) Zeeman effect: [**9 pts**] The script `Assignment3_program_draft_v1.nb` is set up to provide the calculation for the Zeeman effect for all field strengths, as in example 58. Consider only the $|\,2p\,\rangle$ state of Hydrogen. We shall use two different bases for the angular momentum, the total angular momentum basis

$$\mathcal{B}_{tot} = \{|\, j=\frac{3}{2}, m_j=\frac{3}{2}\,\rangle, |\, j=\frac{3}{2}, m_j=\frac{1}{2}\,\rangle, |\, j=\frac{3}{2}, m_j=-\frac{1}{2}\,\rangle,$$
$$|\, j=\frac{3}{2}, m_j=-\frac{3}{2}\,\rangle, |\, j=\frac{1}{2}, m_j=\frac{1}{2}\,\rangle, |\, j=\frac{1}{2}, m_j=-\frac{1}{2}\,\rangle\} \qquad (115)$$

and the separate basis

$$\mathcal{B}_{sep} = \{|\, m_\ell=1, m_s=\frac{1}{2}\,\rangle, |\, m_\ell=1, m_s=-\frac{1}{2}\,\rangle, |\, m_\ell=0, m_s=\frac{1}{2}\,\rangle,$$
$$|\, m_\ell=0, m_s=-\frac{1}{2}\,\rangle, |\, m_\ell=-1, m_s=\frac{1}{2}\,\rangle, |\, m_\ell=-1, m_s=-\frac{1}{2}\,\rangle\} \qquad (116)$$

(a) Revise QM-I, section 4.8., on addition of angular momenta, to figure out what the above means, and based on rules there and QM-II Eqns. (7.84) and (7.85) set up a basis transformation matrix $\underline{\underline{O}}$ such that $\mathcal{B}_{tot} = \underline{\underline{O}}\mathcal{B}_{sep}$. Implement that matrix at one of the XXX in the code, you may use the defined prefactors. [2 pts]
Solution: We use equations (7.85) and (7.86) from QM-II which read.

$$|\left(j=l+\frac{1}{2}\right), l, s, m_j\,\rangle = \sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}}|\, l, s, m_l=m_j-\frac{1}{2}, m_s=\frac{1}{2}\,\rangle$$
$$+\sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}}|\, l, s, m_l=m_j+\frac{1}{2}, m_s=\frac{-1}{2}\,\rangle \qquad (117)$$

$$|\left(j=l-\frac{1}{2}\right), l, s, m_j\,\rangle = -\sqrt{\frac{l-m_j+\frac{1}{2}}{2l+1}}|\, l, s, m_l=m_j-\frac{1}{2}, m_s=\frac{1}{2}\,\rangle$$
$$+\sqrt{\frac{l+m_j+\frac{1}{2}}{2l+1}}|\, l, s, m_l=m_j+\frac{1}{2}, m_s=\frac{-1}{2}\,\rangle \qquad (118)$$

From now on we will skip writing l and s in the states for typographical convenience and write the states in the format: $|\, j, m_j\,\rangle$ and $|\, m_l, m_s\,\rangle$. The total angular momentum states can be expressed in terms of orbital and spin angular momentum states as follows

$$\left|\frac{3}{2},\frac{3}{2}\right\rangle = \left|1,\frac{1}{2}\right\rangle \qquad (119)$$
$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|0,\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|1,\frac{-1}{2}\right\rangle \qquad (120)$$
$$\left|\frac{3}{2},\frac{-1}{2}\right\rangle = \sqrt{\frac{1}{3}}\left|-1,\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|0,\frac{-1}{2}\right\rangle \qquad (121)$$
$$\left|\frac{3}{2},\frac{-3}{2}\right\rangle = \left|-1,\frac{-1}{2}\right\rangle \qquad (122)$$
$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = -\sqrt{\frac{1}{3}}\left|0,\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|1,\frac{-1}{2}\right\rangle \qquad (123)$$
$$\left|\frac{1}{2},\frac{-1}{2}\right\rangle = -\sqrt{\frac{2}{3}}\left|-1,\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|0,\frac{-1}{2}\right\rangle \qquad (124)$$

Expressing $\mathcal{B}_{tot}$ and $\mathcal{B}_{sep}$ as

$$\mathcal{B}_{tot} = \begin{pmatrix} \left|\frac{3}{2},\frac{3}{2}\right\rangle \\ \left|\frac{3}{2},\frac{1}{2}\right\rangle \\ \left|\frac{3}{2},\frac{-1}{2}\right\rangle \\ \left|\frac{3}{2},\frac{-3}{2}\right\rangle \\ \left|\frac{1}{2},\frac{1}{2}\right\rangle \\ \left|\frac{1}{2},\frac{-1}{2}\right\rangle \end{pmatrix}, \qquad \mathcal{B}_{sep} = \begin{pmatrix} \left|1,\frac{1}{2}\right\rangle \\ \left|1,\frac{-1}{2}\right\rangle \\ \left|0,\frac{1}{2}\right\rangle \\ \left|0,\frac{-1}{2}\right\rangle \\ \left|-1,\frac{1}{2}\right\rangle \\ \left|-1,\frac{-1}{2}\right\rangle \end{pmatrix} \tag{125}$$

we get the transformation matrix $\mathcal{O}$

$$\mathcal{B}_{tot} = \mathcal{O}\mathcal{B}_{sep}, \qquad \mathcal{O} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{1}{3}} & -\sqrt{\frac{2}{3}} & 0 \end{pmatrix} \tag{126}$$

(b) We have already used the Hamiltonians $\hat{H}_a$, $\hat{H}_b$, $\hat{H}_c$ from Eq. (7.81) plus Darwin Term and relativistic corrections to find the fine-structure energies in Eq. (7.74). Use that to set up the Matrix Representation of the combination of all these terms in the basis $\mathcal{B}_{tot}$ at XXX for $\hat{H}_{fs}$. [2 pts]
Solution: We already have the eigenvalues E_{nj} for the fine structure Hamiltonian $\hat{H}_{fs}$. Looking at the expression for E_{nj},

$$E_{nj} = E_n \left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \tag{127}$$

we find that these only depend on value of j and n and is independent of m_j. Since $n = 2$ and $l = 1$, j takes two values: $\frac{3}{2}$ and $\frac{1}{2}$. So we have only two distinct eigenvalues which are of course degenerate. The script ***`Assignment3_program_draft_v1.nb`*** *is designed to calculate these or we can do it manually. Based on this it is easy to find the following matrix representation of $\hat{H}_{fs}$*

$$\hat{H}_{fs} = \begin{pmatrix} E_{2,3/2} & 0 & 0 & 0 & 0 & 0 \\ 0 & E_{2,3/2} & 0 & 0 & 0 & 0 \\ 0 & 0 & E_{2,3/2} & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{2,3/2} & 0 & 0 \\ 0 & 0 & 0 & 0 & E_{2,1/2} & 0 \\ 0 & 0 & 0 & 0 & 0 & E_{2,1/2} \end{pmatrix} \tag{128}$$

In the basis $\mathcal{B}_{sep}$ the Hamiltonian $\hat{H}_{fs}$ can be expressed as

$$\hat{H}_{fs}^{\mathcal{B}_{sep}} = \mathcal{O}^{-1}\hat{H}_{fs}^{\mathcal{B}_{tot}}\mathcal{O} \tag{129}$$

(c) We shall ignore $\hat{H}_e$ in Eq. (7.81) but have to add $\hat{H}_d$. This one is easiest expressed in the basis $\mathcal{B}_{sep}$, insert XXX for $\hat{H}_{mag}$. [2 pts]
Solution: The Hamiltonian $\hat{H}_d$ and its eigenvalues are

$$\hat{H}_d = \frac{\mu_B}{\hbar}B(\hat{L}_z + 2\hat{S}_z) \tag{130}$$

$$E_{m_l,m_s} = \mu_B B(m_l + 2m_s) \tag{131}$$

Since the eigenvalues depend only on m_l and m_s it is convenient to work with $\mathcal{B}_{sep}$ basis. The Hamiltonian in this basis reads

$$\hat{H}_d = \mu_B B \begin{pmatrix} 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2 \end{pmatrix} \tag{132}$$

(d) Now combine both contributions into a total Hamiltonian $\hat{H}_{tot} = \hat{H}_{fs} + \hat{H}_{mag}$ at another XXX and execute all the subsequent lines of code that should find eigenvalues and eigenvectors as a function of magnetic field. Discuss all the plots. In particular relate the eigenvectors to the labels of lines in the figures. [3 pts]
Solution: We use Eq. (129) to express $\hat{H}_{fs}$ in $\mathcal{B}_{sep}$ basis. Then we add to this $\hat{H}_d$ to get $\hat{H}_{tot}$. Alternatively one can express $\hat{H}_d$ in $\mathcal{B}_{tot}$ basis.

$$\hat{H}_{tot} = \mathcal{O}^{-1}\hat{H}_{fs}^{\mathcal{B}_{tot}}\mathcal{O} + \hat{H}_d \tag{133}$$

$$\text{or} \quad \hat{H}_{tot} = \hat{H}_{fs} + \mathcal{O}\hat{H}_d^{\mathcal{B}_{sep}}\mathcal{O}^{-1} \tag{134}$$

However we will use Eq. (133) here since the code is designed to work in $\mathcal{B}_{sep}$ basis. The eigenvalues of $\hat{H}_{tot}$ as a function of external magnetic field is given below.
The plots below show how eigenvectors vary with magnetic field. The script file also gives plot for the asymptotic states for vanishing and for very strong magnetic fields. It is clear from the section "Asymptotic eigenstates" of the script file that the state-labels on the figure in Example 58 of QM-II pertain ONLY to either vanishing or very strong magnetic fields. For intermediate strength of magnetic fields it is clear from the plots given above that the eigenstates are superpositions (see the plots for eigenvectors) of various basis states in $\mathcal{B}_{sep}$.

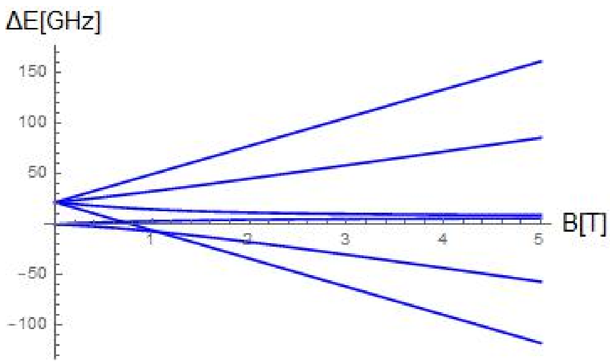

Figure 6: Variation of eigenvalues of $\hat{H}_{tot}$ w.r.t. external magnetic field

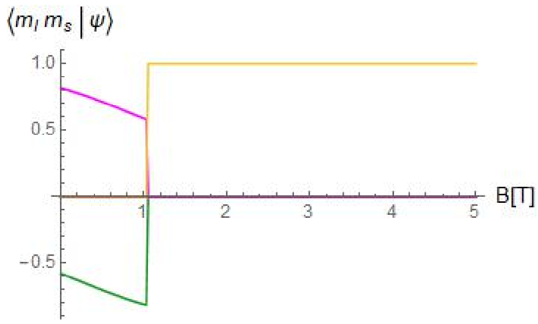

Figure 7: Eigenvector-1

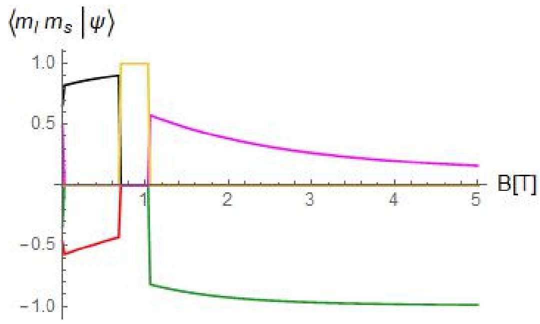

Figure 8: Eigenvector-2

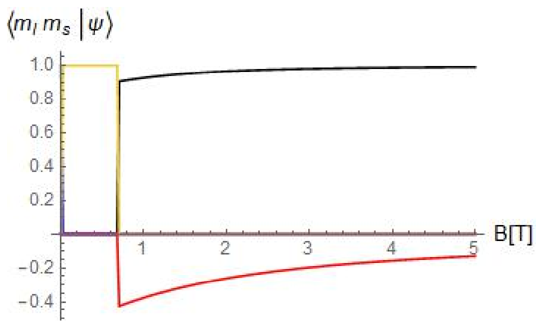

Figure 9: Eigenvector-3

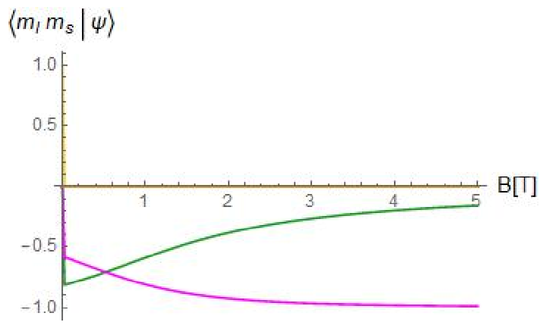

Figure 10: Eigenvector-4

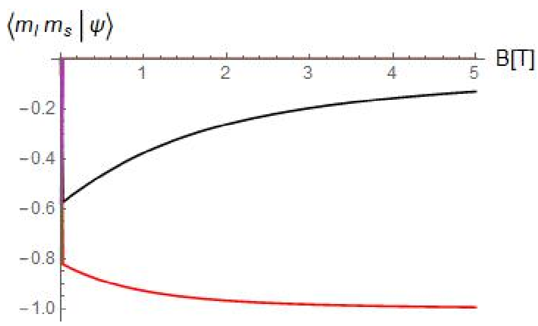

Figure 11: Eigenvector-5

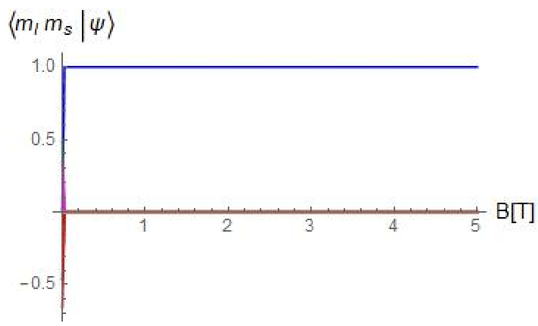

Figure 12: Eigenvector-6

Some additional interpretation of the weak and strong field zeeman effect that you can see discussed in books (Griffith, and simpler, Beiser), is this: for weak magnetic fields spin-orbit coupling first fixes a specific relative alignment of the magnetic moment from the spin and that due to orbital motion such that these two couple into a fixed total angular momentum. The magnetic moment from the total angular momentum j *then has* $2j + 1$ *possible orientations wrt. the magnetic field (different values of* m_j*), such that we get the picture from example 58 for weak field (lines split according to* m_j*). In contrast, for strong fields, we just separately align the spin magnetic moment and orbital magnetic moment in the external field. The possible combinations of those two then give you the five lines on the strong field side of example 58.*

A Identities for binomial coefficients

Consider the expression below for $x < 1$,

$$(1-x)^{-m}(1-x)^{-n} = (1-x)^{-(m+n)} \tag{135}$$

Expanding these in terms of binomial coefficients,

$$\sum_{a,b=0}^{\infty} \binom{m+a-1}{a}\binom{n+b-1}{b} x^{a+b} = \sum_{c=0}^{\infty} \binom{m+n+c-1}{c} x^c \tag{136}$$

Upon comparison of the coefficients of like powers of x gives us $a+b=c$, so that we can take $b = c-a$,

$$\sum_{a=0}^{c} \binom{m+a-1}{a}\binom{n+c-a-1}{c-a} = \binom{m+n+c-1}{c} \tag{137}$$

Upon redefining the variables m and n we can rewrite this as follows which is known as Chu–Vandermonde identity.

$$\sum_{a=0}^{c} \binom{m+a}{a}\binom{n-a}{c-a} = \binom{m+n+1}{c} \tag{138}$$

When $n = c$ we get

$$\sum_{a=0}^{c} \binom{m+a}{a} = \binom{m+c+1}{c} \tag{139}$$

which is the "hockey-stick identity" (23).
When $n = k$ and $c = k-1$ we get

$$\sum_{a=0}^{k-1} (k-a)\binom{m+a}{a} = \binom{m+k+1}{k-1} \tag{140}$$

When $n = k+1$ and $c = k-1$ we get

$$\sum_{a=0}^{k-1} \frac{(k-a+1)(k-a)}{2}\binom{m+a}{a} = \binom{m+k+2}{k-1} \tag{141}$$

Upon expanding this we see that

$$\sum_{a=0}^{k-1} (k-a)^2\binom{m+a}{a} + \sum_{a=0}^{k-1} (k-a)\binom{m+a}{a} = 2\binom{m+k+2}{k-1} \tag{142}$$

Using Eq. (140) in the above equation we get

$$\sum_{a=0}^{k-1} (k-a)^2\binom{m+a}{a} = 2\binom{m+k+2}{k-1} - \binom{m+k+1}{k-1} \tag{143}$$

$$= \frac{(m+2k+1)(m+k+1)!}{(k-1)!(m+3)!} \tag{144}$$