PH 422: Quantum Mechanics II
Tutorial Sheet 4

This tutorial sheet contains problems related to the perturbation theory for time-independent Schrödinger equation.

1. Assume that a particle of mass m, is carrying out simple harmonic motion in the x direction.

   (a) If the particle carries a charge q, and it is exposed to an electric field E_0 in the x direction, obtain its exact eigenvalues and eigenvectors. In particular, show that the exact eigenket for the n-th level $|\psi_n\rangle$ is related to that of the unperturbed state $|\psi_n^{(0)}\rangle$, by $|\psi_n\rangle = e^{-iqE_0p/m\omega^2\hbar}|\psi_n^{(0)}\rangle$, where p is the momentum operator.

   (b) Assuming that the electric field is small, treat the extra term in the Hamiltonian $V = -qE_0x$ as a small perturbation, to calculate:

      i. corrections to the energy eigenvalues up to second order in perturbation theory

      ii. corrections to the wave functions up to first order in perturbation theory.

   (c) Expand your exact results in leading orders in $\mathcal{E}_0$, and compare them with the results obtained in part (b).
   Soln: Done in the lectures

2. Consider a hydrogen atom in its $1s$ ground state. If we apply an electric field of strength E_0 in the z direction on the hydrogen atom, make an estimate of the first non-vanishing order of correction in the energy of the $1s$ state, due to the presence of the electric field. Using this, estimate the static polarizability α of the atom, employing the formula

$$\alpha = -\left(\frac{\partial^2 \Delta E}{\partial E_0^2}\right)_{E_0=0},$$

   where ΔE is the shift in the energy of the atom, due to the presence of the external electric field. This effect is called quadratic stark effect.
   Soln: Done in the lectures

3. Consider a 1D SHO with particle mass m, and frequency ω, with the Hamiltonian $H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$. To this Hamiltonian we add a perturbing term $V = \frac{1}{2}\epsilon m\omega^2x^2$, where $\epsilon \ll 1$.

   (a) Solve this problem exactly, and expand the energies to the second order in ϵ, and wave functions to the first order in ϵ.

   (b) Calculate, using the perturbation theory, the energy corrections to the second order in ϵ, and wave functions to first order in ϵ, treating V as a perturbation. For the wave function, perform the calculations only for the ground state. Compare your results to those obtained in part (b).

Soln: Here

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{1}$$

and the perturbation term

$$V = \frac{1}{2}\epsilon m\omega^2 x^2 \tag{2}$$

$$\Rightarrow H = H_0 + V = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(1+\epsilon)x^2$$

$$\Rightarrow H = \frac{p^2}{2m} + \frac{1}{2}m\omega'^2 x^2 \tag{3}$$

where

$$\omega' = \omega\sqrt{1+\epsilon} \tag{4}$$

Obviously the exact eigenvalues and eigenfuntions of H

$$H|\psi_n\rangle = E_n|\psi_n\rangle \tag{5}$$

are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega'$$

and

$$\psi_n(x) = \psi_n^{(0)}\left(x, \omega \to \omega'\right) \tag{6}$$

Let us expand E_n and $\psi_n(x)$ in power of ϵ to compare it with the perturbation treatment. Clearly

$$\omega' = \omega\sqrt{1+\epsilon} = \omega\left(1+\epsilon\right)^{\frac{1}{2}}$$

or

$$\omega' = \omega\left\{1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{8} + \cdots\right\} \tag{7}$$

$$\Rightarrow E_n = \left(n + \frac{1}{2}\right)\hbar\omega' \tag{8}$$

$$E_n = E_n^{(0)}\left\{1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{8} + \cdots\right\} \tag{9}$$

where $E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega$
We perform the wave function calculation only for $n = 0$.

$$\psi_0(x) = \left(\frac{m\omega'}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{m\omega'}{2\hbar}x^2} \tag{10}$$

Now $(\omega')^{1/4} = \omega^{1/4}(1+\epsilon)^{1/8}$
So, to first order in ϵ

$$\begin{aligned} \omega'^{1/4} &= \omega^{1/4}\left(1+\frac{\epsilon}{8}+\cdots\right) \\ \omega' &= \omega\left(1+\frac{\epsilon}{2}+\cdots\right) \end{aligned} \tag{11}$$

Using Eqn.(11) in Eqn.(10)

$$\begin{aligned} \psi_0(x) &\approx \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{1+\frac{\epsilon}{8}\right\}e^{-\frac{m\omega}{2\hbar}\left\{1+\frac{\epsilon}{2}\right\}x^2} \\ &\approx \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{1+\frac{\epsilon}{8}\right\}e^{-\frac{m\omega}{2\hbar}x^2}e^{-\frac{m\omega\epsilon}{4\hbar}x^2} \end{aligned}$$

Expanding the last term in powers of ϵ and retaining only the last term.

$$\begin{aligned} \psi_0(x) &\approx \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{1+\frac{\epsilon}{8}\right\}\left(1-\frac{m\omega\epsilon}{4\hbar}x^2\right)e^{-\frac{m\omega}{2\hbar}x^2} \\ &\approx \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{1+\frac{\epsilon}{8}-\frac{m\omega\epsilon}{4\hbar}x^2\right\}e^{-\frac{m\omega}{2\hbar}x^2} \\ &\approx \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}-\frac{\epsilon}{4}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{\frac{m\omega}{\hbar}x^2-\frac{1}{2}\right\}e^{-\frac{m\omega}{2\hbar}x^2} \\ &\approx \psi_0^{(0)}(x)-\frac{\epsilon}{16}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\left\{\frac{4m\omega}{\hbar}x^2-2\right\}e^{-\frac{m\omega}{2\hbar}x^2} \end{aligned}$$

but $\frac{4m\omega}{\hbar}x^2-2 = H_2\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$
and using the fact that

$$\boxed{\psi_0(x) \approx \psi_0^{(0)}(x) - \frac{\epsilon}{4\sqrt{2}}\psi_2^{(0)}(x)} \tag{12}$$

Let us now perform perturbation theoretic calculation, using V as perturbation (a). Energy Eigenvalues:

$$\begin{aligned} E_n =& E_n^{(0)} + \langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle \\ &+ \sum_k \frac{|\langle\psi_k^{(0)}|V|\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - {E_k}^{(0)}} \end{aligned}$$

$$\begin{aligned} E_n^{(1)} &= \langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle = \frac{\epsilon}{2}m\omega^2\langle n\left|x^2\right|n\rangle \\ &= \frac{\epsilon}{2}m\omega^2\sum_k\langle n|x|k\rangle\langle k|x|n\rangle \end{aligned}$$

but

$$\langle k|x|n\rangle = \langle n|x|k\rangle = \sqrt{\frac{\hbar}{m\omega}}\left[\sqrt{\frac{n}{2}}\delta_{k,n-1}+\sqrt{\frac{n+1}{2}}\delta_{k,n+1}\right]$$

$$\sum_k x_{kn}x_{nk} = \frac{\hbar}{m\omega}\left\{\frac{n}{2}\sum_k \delta_{n-1,k}\delta_{k,n-1} + \frac{n+1}{2}\sum_k \delta_{n+1,k}\delta_{k,n+1}\right\}$$

$$\sum_k x_{kn}x_{nk} = \frac{\hbar}{m\omega}\left\{\frac{n}{2}\sum_k \delta_{n-1,k}\delta_{k,n-1} + \frac{n+1}{2}\sum_k \delta_{n+1,k}\delta_{k,n+1} + 2\sqrt{\frac{n(n+1)}{4}}\sum_k \delta_{n-1,k}\delta_{k,n+1}\right\}$$

but

$$\sum_k \delta_{n\pm1,k}\delta_{k,n\pm1} = \delta_{n\pm1}\delta_{n\pm1} = 1$$

$$\sum_k \delta_{n\pm1,k}\delta_{k,n\mp1} = \delta_{n\pm1}\delta_{n\mp1} = 0$$

$$\Rightarrow \boxed{E_n^{(1)} = \frac{\epsilon}{2}\left(n+\frac{1}{2}\right)\hbar\omega = \frac{\epsilon}{2}E_n^{(0)}}$$

$$E_n^{(2)} = \sum_{k\neq n}\frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} = \frac{\epsilon^2}{4}m^2\omega^4\sum_{k\neq n}\frac{|\langle k\left|x^2\right|n\rangle|^2}{\left(n+\frac{1}{2}\right)\hbar\omega - \left(k+\frac{1}{2}\right)\hbar\omega}$$

$$= \frac{\hbar}{m\omega}\sqrt{\frac{n}{2}}\delta_{k,n-1} + \sqrt{\frac{n+1}{2}}\delta_{k,n+1}$$

Now

$$\langle k\left|x^2\right|n\rangle = \sum_l \langle k|x|l\rangle\langle l|x|n\rangle$$

$$= \frac{\hbar}{m\omega}\sum_l\left(\sqrt{\frac{k}{2}}\delta_{l,k-1} + \sqrt{\frac{k+1}{2}}\delta_{l,k+1}\right)\times\left(\sqrt{\frac{n}{2}}\delta_{l,n-1} + \sqrt{\frac{n+1}{2}}\delta_{l,n+1}\right)$$

$$= \frac{\hbar}{m\omega}\left\{\sqrt{\frac{kn}{4}}\delta_{k-1,n-1} + \sqrt{\frac{(k+1)(n+1)}{4}}\delta_{k+1,n+1} \sqrt{\frac{(k+1)(n)}{4}}\delta_{k+1,n-1} + \sqrt{\frac{k(n+1)}{4}}\delta_{k-1,n+1}\right\}$$

$$x_{kn}^2 = \frac{\hbar}{m\omega}\left\{\left(n+\frac{1}{2}\right)\delta_{k,n} + \frac{\sqrt{n(n-1)}}{2}\delta_{k,n-2} + \frac{\sqrt{(n+1)(n+2)}}{2}\delta_{k,n+2}\right\} \tag{13}$$

$$\Rightarrow E_n^{(2)} = \frac{\epsilon^2}{4} m^2\omega^4 \frac{\langle n-2\,|x^2|\,n\rangle^2}{2\hbar\omega} + \frac{\epsilon^2}{4} m^2\omega^4 \frac{|\langle n+2|x|n\rangle|^2}{(-2\hbar\omega)}$$
$$= \frac{\epsilon^2}{4}\frac{m^2\omega^4}{2\hbar\omega}\frac{\hbar^2}{m^2\omega^2}\frac{n(n-1)}{4} - \frac{\epsilon^2}{4}\frac{m^2\omega^4}{2\hbar\omega}\frac{\hbar^2}{m^2\omega^2}\frac{(n+1)(n+2)}{4}$$
$$= -\frac{\epsilon^2}{8}\frac{(4n+2)}{4}\hbar\omega = -\frac{\epsilon^2}{8}\left(n+\frac{1}{2}\right)\hbar\omega$$
$$= -\frac{\epsilon^2}{8}E_n^{(0)}$$

Collecting the results to second order

$$\boxed{E_n = \left(1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{8}\right) E_n^{(0)}} \tag{14}$$

which is identical to Eq. (9).
(b). Wave Function: First order correction

$$\left|\psi_n^{(1)}\right\rangle = \sum_{k\neq n} \left|\psi_k^{(0)}\right\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}$$
$$= \sum_{k\neq n} \left|\psi_k^{(0)}\right\rangle \frac{\frac{1}{2}m\omega^2\epsilon\,\langle k\,|x^2|\,n\rangle}{(n-k)\hbar\omega}$$

Using Eq.( )

$$\left|\psi_n^{(1)}\right\rangle = \frac{\left|\psi_{n-2}^{(0)}\right\rangle \frac{\sqrt{n(n-1)}}{2}\frac{m\omega^2\epsilon}{2}\frac{\hbar}{m\omega}}{2\hbar\omega} - \frac{\left|\psi_{n+2}^{(0)}\right\rangle \frac{\sqrt{(n+1)(n+2)}}{2} m\omega^2\epsilon\frac{\hbar}{m\omega}}{2\hbar\omega}$$

$$\boxed{\left|\psi_n^{(1)}\right\rangle = \frac{\epsilon}{8}\sqrt{n(n-1)}\left|\psi_{n-2}^{(0)}\right\rangle - \frac{\epsilon}{8}\sqrt{(n+1)(n+2)}\left|\psi_{n+2}^{(0)}\right\rangle}$$

for $n = 0$, we have

$$\left|\psi_0^{(1)}\right\rangle = \frac{-\epsilon}{4\sqrt{2}}\left|\psi_2^{(0)}\right\rangle$$

which is identical to the $O(\epsilon)$ term in Eq.(12).

4. Consider a 1D SHO with particle mass m, and frequency ω. Assume that the Hamiltonian is perturbed by a term $V = \lambda x^3$, where λ is a small number. Calculate the perturbation corrections to energy up to second order, and to the wave functions, up to the first order.
Soln: Easy to do

5. Consider a hydrogen atom in its first excited state with principal quantum number $n = 2$. If we apply an electric field $\mathbf{E} = E_0\hat{k}$ (E_0 is a constant) on the atom, using the degenerate perturbation theory, calculate the first order corrections to the energy, and the modified zeroth order wave functions. What happens to the four-fold degeneracy of this level?
Soln: Done in the lectures

6. Consider a particle in a two-dimensional box with the potential

$$V_0 = \begin{cases} 0 & \text{for } 0 \le x \le a,\ 0 \le y \le a \\ \infty & \text{otherwise.} \end{cases}$$

What are the energy eigenvalues and eigenfunctions for this system? If we add a perturbation term V to this Hamiltonian, defined by

$$V = \begin{cases} \lambda xy & \text{for } 0 \le x \le a,\ 0 \le y \le a \\ 0 & \text{otherwise.} \end{cases}$$

Obtain the zeroth order energy eigenfunctions, and the first-order energy shifts to the ground and the first excited states.
Soln: For a two-dimensional square box, the eigenvalues and eigenfunctions are given by

$$E_{n,m} = \frac{\hbar^2\pi^2}{2ma^2}\left(n^2 + m^2\right)$$

$$\psi_{n,m}(x,y) = \frac{2}{a}\sin\frac{n\pi x}{a}\sin\frac{m\pi y}{a}$$

and here perturbation term is

$$V = \lambda xy \quad for \quad 0 \leqslant x \leqslant a,\ 0 \le y \le a$$

Next we consider corrections to the ground state and the first excited state.
(I). Ground state corrections: Ground state unperturbed wave function corresponds to $n = m = 1$

$$\psi^{(0)}_{11}(x,y) = \frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{\pi y}{a}$$

and energy

$$E^{(0)}_{11} = \frac{\hbar^2\pi^2}{ma^2} \tag{15}$$

(i) Energy Corrections:

$$E^{(1)}_{11} = \left\langle \psi^{(0)}_{11}|V|\psi^{(0)}_{11}\right\rangle$$

For computing various terms, it is important to calculate following useful integral

$$\begin{aligned} I_{n,m} &= \int_0^a x\sin\frac{n\pi x}{a}\frac{m\pi x}{a}dx \quad for\ (n \neq m) \\ &= \frac{1}{2}\int_0^a \left[x\cos(n-m)\frac{\pi x}{a} - x\cos(n+m)\frac{\pi x}{a}\right]dx \end{aligned}$$

Now

$$\begin{aligned} \int x\cos\alpha x dx &= \frac{1}{\alpha}x\sin\alpha x - \frac{1}{\alpha}\int \sin\alpha x dx \\ &= \frac{x\sin\alpha x}{\alpha} + \frac{\cos\alpha x}{\alpha^2} \end{aligned}$$

With this

$$\int_0^a x\cos\frac{n\pi x}{a}dx = \frac{a}{n\pi}x\sin\frac{n\pi x}{a}dx + \frac{a^2}{n^2\pi^2}\cos\frac{n\pi x}{a}\Bigg|_0^a$$
$$= \frac{a^2}{n^2\pi^2}(\cos n\pi - 1)$$
$$\Rightarrow \int_0^a x\cos\frac{n\pi x}{a}dx = \frac{a^2}{n^2\pi^2}\left((-1)^n - 1\right) \tag{16}$$

Using this, we have

$$I_{n,m} = \frac{a^2}{2(n-m)^2\pi^2}\left\{(-1)^{n-m} - 1\right\} - \frac{a^2}{2\left(n^2+m\right)^2\pi^2}\left\{(-1)^{n+m} - 1\right\} \quad for\, n \neq m \tag{17}$$

But

$$I_{n,n} = \frac{1}{2}\int_0^a \left\{x - x\cos\frac{2n\pi x}{a}\right\}dx$$
$$= \frac{x^2}{4}\Bigg|_0^a - \frac{1}{2}\int_0^a x\cos\frac{2n\pi x}{a}dx$$

using Eq.(16) , the second term becomes zero, so that

$$\boxed{I_{n,n} = \frac{a^2}{4}} \tag{18}$$

Now

$$E_{11}^{(1)} = \left(\frac{2}{a}\right)^2 \lambda \int_0^a x\sin^2\frac{\pi x}{a}dx \int_0^a y\sin^2\frac{\pi y}{a}dy$$
$$= \lambda\frac{4}{a^2}I_{11} \times I_{11} = \lambda\frac{4}{a^2} \times \frac{a^2}{4} \times \frac{a^2}{4}$$
$$\Rightarrow \boxed{E_{11}^{(1)} = \frac{\lambda a^2}{4}} \tag{19}$$

(II). First excited state: First excited state of this is two-fold degenerate with energy

$$E_1^{(0)} = E_{2,1} = E_{1,2} = \frac{5\hbar^2\pi^2}{2ma^2} \tag{20}$$

with two eigenfunctions

$$\begin{aligned}\phi_1 &= \psi_{2,1}(x,y) = \frac{2}{a}\sin\frac{2\pi x}{a}\sin\frac{\pi y}{a} \\ \phi_2 &= \psi_{1,2}(x,y) = \frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{2\pi y}{a}\end{aligned} \tag{21}$$

We have to use degenerate perturbation theory at the first order for which we have calculate and diagonalize the V Matrix in $\{\phi_1, \phi_2\}$ basis, with

$$V_{ij} = \langle \phi_i | V | \phi_j \rangle$$

It is obvious that

$$\begin{aligned} V_{11} &= \frac{4\lambda}{a^2} \int_0^a x \sin^2 \frac{2\pi x}{a} dx \int_0^a y \sin^2 \frac{\pi y}{a} dy \\ &= \frac{4\lambda}{a^2} I_{22} I_{11} = \frac{4\lambda}{a^2} \times \left(\frac{a}{2}\right)^2 \times \left(\frac{a}{2}\right)^2 \\ &= \frac{\lambda a^2}{4} \end{aligned}$$

similarly

$$V_{22} = \frac{4\lambda}{a^2} I_{11} I_{22} = \frac{\lambda a^2}{4}$$

and

$$V_{12} = V_{21} = \frac{4\lambda}{a^2} I_{21} I_{12}$$

From Eq.(17)

$$I_{12} = I_{21} = -\frac{a^2}{\pi^2} + \frac{a^2}{9\pi^2}$$

or

$$I_{12} = I_{21} = -\frac{8a^2}{9\pi^2}$$

$$\Rightarrow V_{12} = V_{21} = \frac{256\lambda a^2}{81\pi^4}$$

so that

$$\tilde{V} = \begin{pmatrix} \frac{\lambda a^2}{4} & \frac{256}{81}\frac{\lambda a^2}{\pi^4} \\ \frac{256\lambda a^2}{81\pi^4} & \frac{\lambda a^2}{4} \end{pmatrix}$$

Its characteristic polynomial is

$$\begin{aligned} &k\left(\tfrac{\lambda a^2}{4} - E\right)^2 - \left(\tfrac{256 a^2 \lambda}{81\pi^4}\right)^2 = 0 \\ &\Rightarrow E - \tfrac{\lambda a^2}{4} = \pm \tfrac{256 a^2 \lambda}{81\pi^4} \end{aligned}$$

$$E^{(0)}_{1,2} = \frac{\lambda a^2}{4} \pm \frac{256\lambda a^2}{81\pi^4}$$

Thus the first order correction in energies are

$$\Rightarrow E^{(1)}_1 = \lambda a^2 \left(\frac{1}{4} + \frac{256}{81\pi^4}\right)$$

and

$$\Rightarrow E^{(1)}_2 = \lambda a^2 \left(\frac{1}{4} - \frac{256}{81\pi^4}\right)$$

and easy to verify that the corresponding zeroth order wave functions, which are nothing but eigenfunctions of $\tilde{V}$ are

$$\left|\psi_1^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle + |\phi_2\rangle\right)$$
$$\left|\psi_2^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle - |\phi_2\rangle\right)$$

7. A p-orbital electron characterized by $|n, l = 1, m = \pm 1, 0\rangle$ (ignore spin) is subjected to a potential

$$V = \lambda(x^2 - y^2), \qquad (\lambda = \text{constant}).$$

Obtain the correct zeroth-order energy eigenstates that diagonalize the perturbation. You need not evaluate the energy shifts in detail, but show that the original threefold degeneracy is now completely removed.

Soln: Here we have a three-fold degeneracy of the p level, with the unperturbed eigenfunctions being, in the $|lm\rangle$ notation

$$|\phi_1\rangle = |11\rangle$$
$$|\phi_2\rangle = |10\rangle$$
$$|\phi_3\rangle = |1-1\rangle$$

We have to construct and diagonalize V matrix in this basis, with matrix elements defined as

$$V_{ij} = \langle\phi_i|V|\phi_j\rangle$$

We will calculate these using the Wigner-Eckart theorem. We had showed earlier

$$x^2 - y^2 = \frac{1}{2}\left(T_2^2 + T_2^{-2}\right)$$

with this

$$\begin{aligned} V_{ij} &= \left\langle \alpha_i 1 m_i \left| \frac{\lambda}{2}\left(T_2^2 + T_2^{-2}\right)\right| \alpha_j 1 m_j \right\rangle \\ &= \frac{\lambda}{2}\left\langle 1 m_i \left| T_2^2 \right| 1 m_j \right\rangle + \frac{\lambda}{2}\left\langle 1 m_i \left| T_2^{-2} \right| 1 m_j \right\rangle \end{aligned}$$

using the Wigner-Eckart theorem we have

$$\left\langle 1 m_i \left| T_2^2 \right| 1 m_j \right\rangle = \langle 12 m_j 2 | 121 m_i\rangle \langle 1||T_2||1\rangle$$

clearly this matrix element is non-zero only if

$$m_j + 2 = m_i$$

which is possible if $m_j = -1$ and $m_i = 1$

Similarly

$$\left\langle 1 m \left| T_2^{-2} \right| 1 m_j \right\rangle = \langle 12 m_j - 2 | 121 m_i\rangle \langle 1||T_2||1\rangle$$

this is non-zero only if $m_j - 2 = m_i$, which is possible only for $m_j = 1, m_i = -1$
Rest of the matrix elements of V are zero. If we define the reduced matrix element as $a = \langle 1||T_2||1\rangle$.
The non-zero matrix elements of V are

$$\begin{aligned} V_{13} = \langle \phi_1|V|\phi_3\rangle &= \frac{\lambda}{2}\langle 12-12|1211\rangle\, a \\ &= \left(\sqrt{\frac{3}{5}}\right)\frac{\lambda}{2}a = \sqrt{\frac{3}{5}}\frac{\lambda a}{2} \end{aligned}$$

Similarly

$$\begin{aligned} V_{31} = \langle \phi_3|V|\phi_1\rangle &= \frac{\lambda a}{2}\langle 121-2|121-1\rangle \\ &= \sqrt{\frac{3}{5}}\frac{\lambda a}{2} \end{aligned}$$

$$\Rightarrow V = \frac{\lambda a}{2}\sqrt{\frac{3}{5}}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

Let's compute the characteristic polynomial

$$\begin{vmatrix} -\varepsilon & 0 & 1 \\ 0 & -\varepsilon & 0 \\ 1 & 0 & -\varepsilon \end{vmatrix} = 0$$

$$\begin{aligned} -\varepsilon\left(\varepsilon^2 - 0\right) + (0+\varepsilon) &= 0 \\ +\varepsilon - \varepsilon^3 &= 0 \\ \Rightarrow \varepsilon\left(\varepsilon^2 - 1\right) &= 0 \end{aligned}$$

so three eigenvalues will be

$$\varepsilon = 0, \varepsilon = \pm 1$$

which means the first order energy corrections are

$$\triangle E = 0, \Delta E = \pm\sqrt{\frac{3}{5}}\frac{\lambda a}{2}$$

If the the initial energy eigenvalue of p orbitals was E_0, the corrected eigenvalues will be

$$E_1 = E_0, E_2 = E_0 - \frac{\lambda a}{2}\sqrt{\frac{3}{5}}$$

$$E_3 = E_0 + \frac{\lambda a}{2}\sqrt{\frac{3}{5}}$$

Eigenvectors for $\varepsilon = 0$

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

$$\Rightarrow c_1 = c_3 = 0$$

$$\Rightarrow |\psi_1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = |\phi_2\rangle$$

For $\varepsilon_2 = -1, E_2 = E_0 - \frac{\lambda a}{2}\sqrt{\frac{3}{5}}$

$$\begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

$$\Rightarrow c_2 = 0, c_1 = -c_3$$

$$\Rightarrow |\psi_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(|\phi_1\rangle - |\phi_3\rangle\right)$$

easy to show that for $\varepsilon_3 = +1$

$$E_3 = E_0 + \frac{\lambda a}{2}\sqrt{\frac{3}{5}}$$

$$|\psi_3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(|\phi_1\rangle + |\phi_3\rangle\right)$$

8. A Hamiltonian matrix for a two-level system is given by

$$H = \begin{pmatrix} E_1^0 & \lambda\Delta \\ \lambda\Delta & E_2^0 \end{pmatrix}.$$

Clearly, the energy eigenfunctions for the unperturbed problem ($\lambda = 0$) are given by

$$\phi_1^{(0)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \phi_2^{(0)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

(a) Solve this problem exactly to find the energy eigenfunctions ψ_1 and ψ_2, and the energy eigenvalues E_1 and E_2.

(b) Assuming that $\lambda|\Delta| \ll |E_1^0 - E_2^0|$, solve the same problem using perturbation theory up to first order in the energy eigenfunctions and up to second order in energy eigenvalues. Compare with the exact results obtained in part (a).

(c) Suppose that the two unperturbed energies are "almost degenerate," that is

$$|E_1^0 - E_2^0| \ll \lambda|\Delta|.$$

Show that the exact results of part (a) closely resemble what you would expect by applying degenerate perturbation theory to this problem with $E_1^0 = E_2^0$.

Soln: Attempt on your own

9. When a magnetic field $\mathbf{B} = B\hat{k}$, is applied to a hydrogen atom, it leads to the addition of the following perturbation term to its Hamiltonian

$$V = -\frac{eB}{2mc}(L_z + 2S_z),$$

where c is the speed of light, e is the charge of the electron, m its mass, while L_z and S_z, respectively, are the components of the z component of its orbital and spin angular momenta. Using the first-order perturbation theory, calculate the energy shifts due to this term when the hydrogen atom is in: (a) an s state, and (b) in a p state. This shift in energy levels due to an external magnetic field is called the Zeeman effect.
Soln: We will consider two cases of Zeeman shift, with and without considering spin.
(I). Without spin:
In this case

$$V = \frac{-eBL_z}{2mc}$$

(i) **s level**
In $|lm\rangle$ form at an s level is donated as $|00\rangle$

$$\Rightarrow \Delta E_S^{(1)} = -\frac{eB}{2mC}\langle 00|L_z|00\rangle$$

but $L_z|00\rangle = 0$

$$\Rightarrow \Delta E_s^{(1)} = 0$$

$\Rightarrow$no Zeeman shift for s level without taking spin into account.
(ii). **p level**: Here we have three degenerate states $|11\rangle, |10\rangle, |1-1\rangle$
Using the fact that

$$L_z|lm\rangle = m\hbar|lm\rangle$$

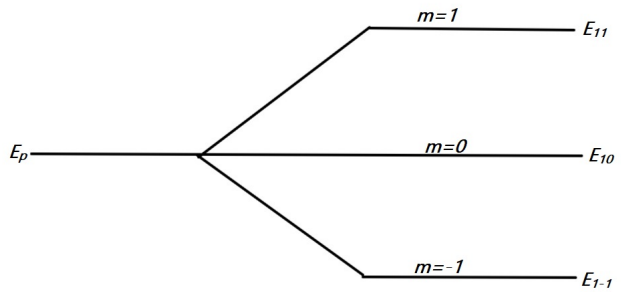
and defining Bohr magneton

$$\mu_B = \frac{-e\hbar}{2mc}$$

we have the energy corrections to the three states

$$\Delta E_{lm}^{(1)} = \langle lm|V|lm\rangle$$
$$\Delta E_{lm}^{(1)} = \mu_B Bm$$

Therefore, the splitting of the p level will be shown, with total energy being $E_{lm} = E_p + \Delta E_{lm}^{(1)}$



(II). With spin
Here

$$V = \frac{-eB}{2mc}\left(L_z + 2S_z\right)$$

(i) **s level:**
Now we have two eigenfunctions with uncoupled states $|l\frac{1}{2}mS_z\rangle$ as the basis

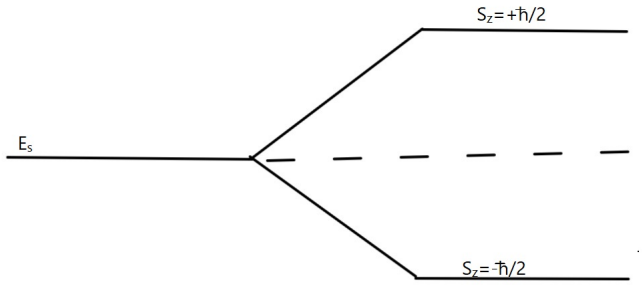
$$\begin{aligned} |\phi_1\rangle &= \left| \begin{array}{cccc} 0 & \frac{1}{2} & 0 & \frac{1}{2} \end{array} \right\rangle \\ |\phi_2\rangle &= \left| \begin{array}{cccc} 0 & \frac{1}{2} & 0 & -\frac{1}{2} \end{array} \right\rangle \end{aligned}$$

so first order energy corrections will be

$$\begin{aligned} E^{(1)}_{S_{1/2}} &= \langle\phi_1|V|\phi_1\rangle = -\frac{eB}{2mc}\left(2\frac{\hbar}{2}\right) \\ &= \mu_B B \end{aligned}$$

and

$$E^{(1)}_{S_{-1/2}} = \langle\phi_2|V|\phi_2\rangle = -\mu_B B$$



(ii). **p level**: Including spin, now we have six basic steps of the form $|lsmS_z\rangle \equiv |1\frac{1}{2}mS_z\rangle$

$$\begin{aligned} |\phi_1\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & 1 & \frac{1}{2} \end{array} \right\rangle \\ |\phi_2\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & 1 & -\frac{1}{2} \end{array} \right\rangle \\ |\phi_3\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & 0 & \frac{1}{2} \end{array} \right\rangle \\ |\phi_4\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & 0 & -\frac{1}{2} \end{array} \right\rangle \\ |\phi_5\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & -1 & \frac{1}{2} \end{array} \right\rangle \\ |\phi_6\rangle &= \left| \begin{array}{cccc} 1 & \frac{1}{2} & -1 & -\frac{1}{2} \end{array} \right\rangle \end{aligned}$$

and perturbation correction is

$$\begin{aligned} \Delta E^{(1)}_{(i)} &= \langle\phi_i|V|\phi_i\rangle \\ \Rightarrow \Delta E^{(1)}_{(i)} &= \mu_B B\left(m_i + m_{si}\right) \\ &\text{where } m_i = 0, \pm 1, \;\; m_{si} = \pm 1 \quad \text{for} \quad s_z = \pm\frac{\hbar}{2} \end{aligned}$$

This splitting can be shown as