Problem Set 7.

Practice problems for time independent perturbation theory I

PH3101 - QM II
Sem 1, 2017 - 2018

1. Calculate the first order correction to the ground state energy of a simple harmonic oscillator due to an anharmonic perturbation $\hat{H}' = bx^4$. Assume that b is small.
(Hint: Use raising and lowering operators.)

2. Calculate the first and second order energy corrections to the ground state energy of a charged particle with charge q in an infinite square well $x \in \left[-\frac{a}{2}, \frac{a}{2}\right]$ due a weak external electric field $\hat{H}' = qEx$.

3. *Problem 8.6 of Quantum Mechanics by Bransden and Joachain*
Consider a one-dimensional linear harmonic oscillator perturbed by a Gaussian perturbation $\hat{H}' = \lambda\, e^{-ax^2}$. Calculate the first-order correction to the ground-state energy only.
(Hint: You may find using the ground state wavefunction is simpler here.)

4. *Problem 8.7 of Quantum Mechanics by Bransden and Joachain*
Consider an electron in the electrostatic field of a nucleus of charge Ze. Let the nuclear charge be distributed uniformly within a sphere of radius R, so that the electrostatic potential due to the nucleus is

$$V(r) = \begin{cases} \frac{Ze^2}{(4\pi\varepsilon_0)2R}\left(\frac{r^2}{R^2} - 3\right), & \text{for } r \le R \\ -\frac{Ze^2}{(4\pi\varepsilon_0)r}, & \text{for } r > R \end{cases} \tag{1}$$

Taking the unperturbed Hamiltonian to be the hydrogenic Hamiltonian $\hat{H}_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}$ and the perturbation to be the difference between $V(r)$ and the Coulomb interaction $-\frac{Ze^2}{(4\pi\varepsilon_0)r}$.

(a) Show that the first-order energy shift due to this perturbation is

$$\Delta E = \frac{Ze^2}{(4\pi\varepsilon_0)2R}\int_0^R [R_{nl}(r)]^2\left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr \tag{2}$$

where $R_{nl}(r)$ is a radial hydrogenic wave function.

(b) Taking $R_{nl}(r) \simeq R_{nl}(0)$ inside the nucleus, show that

$$\Delta E = \frac{e^2}{(4\pi\varepsilon_0)}\frac{2}{5}R^2\frac{Z^4}{a_\mu^3 n^3}\delta_{l0}\,. \tag{3}$$

5. Consider a quantum mechanical system described by the Hamiltonian

$$\hat{H} = E_0\begin{pmatrix} -5 & 3\varepsilon & 0 & 0 \\ 3\varepsilon & 5 & 0 & 0 \\ 0 & 0 & 8 & -\varepsilon \\ 0 & 0 & -\varepsilon & -8 \end{pmatrix}, \tag{4}$$

where ε is small.

(a) Write the Hamiltonian as $\hat{H} = \hat{H}_0 + \hat{H}'$! Find the eigenvalues and eigenvectors of $\hat{H}_0$.

(b) ~~Diagonalize $\hat{H}$ to~~ find exact eigenvalues of $\hat{H}$. Expand the eigenvalues to second order in ε.

(c) Using perturbation theory, calculate the first and second order corrections to the energy eigenvalues. Compare the results with the exact values obtained in (b).
(Hint: Look at worked out example 9.2 of Quantum Mechanics: Concepts and Applications by Zettili.)

Problem Set 7 Solution

Time Independent Perturbation Theory I

Problem 1 Anharmonic Oscillator - Perturbation of Simple Harmonic Oscillator

A simple harmonic oscillator is given an anharmonic perturbation $\hat{H}' = bx^4$ where b is small. The perturbed Hamiltonian is thus

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}mw^2x^2 + bx^4 = \hat{H}_0 + \hat{H}'$$

where $\hat{H}_0 = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}mw^2x^2$ is the unperturbed Hamiltonian and $\hat{H}' = bx^4$ is the perturbation. The first order correction to the nth energy eigenvalues is given by:

$$\boxed{E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle = H'_{nn}} \tag{1.1}$$

where $\boxed{H'_{ij} = \left\langle \psi_i^{(0)} \middle| H' \middle| \psi_j^{(0)} \right\rangle}$ and $\psi_n^{(0)}$ is the energy eigenfunction of the unperturbed system. That is

"The first order correction to the energy is the expectation value of the perturbation, in the *unperturbed* state."

Recall the ground state energy eigenfunction of simple harmonic oscillator is $\psi_0^{(0)}(x) = \left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{mw}{2\hbar}x^2}$. Therefore the first order correction to the ground state energy is:

$$E_0^{(1)} = H'_{00} = \left\langle \psi_0^{(0)} \middle| H' \middle| \psi_0^{(0)} \right\rangle = \left\langle \psi_0^{(0)} \middle| bx^4 \middle| \psi_0^{(0)} \right\rangle = b\sqrt{\frac{mw}{\pi\hbar}} \int_{-\infty}^{\infty} x^4 e^{-\frac{mw}{\hbar}x^2} dx = 2b\sqrt{\frac{mw}{\pi\hbar}} \int_0^{\infty} x^4 e^{-\frac{mw}{\hbar}x^2} dx$$

$$= 2b\sqrt{\frac{mw}{\pi\hbar}} \left(\frac{\hbar}{2mw}\right) \int_0^{\infty} \left(\frac{\hbar}{mw}y\right)^{\frac{3}{2}} e^{-y} dy = \frac{b}{\sqrt{\pi}}\left(\frac{\hbar}{mw}\right)^2 \int_0^{\infty} y^{\frac{3}{2}} e^{-y} dy = \frac{b}{\sqrt{\pi}}\left(\frac{\hbar}{mw}\right)^2 \Gamma\left(\frac{5}{2}\right)$$

$$= \frac{b}{\sqrt{\pi}}\left(\frac{\hbar}{mw}\right)^2 \left(\frac{3}{4}\sqrt{\pi}\right) = 3b\left(\frac{\hbar}{2mw}\right)^2$$

where we have use the fact that $x^4 e^{-\frac{mw}{\hbar}x^2}$ is an even function, the substitution $y = \frac{mw}{\hbar}x^2 \Longrightarrow \frac{dy}{dx} = \frac{2mw}{\hbar}x$, the gamma function $\Gamma(z) = \int_0^{\infty} y^{z-1}e^{-y}dy$ and its result $\Gamma\left(\frac{5}{2}\right) = \frac{3}{4}\sqrt{\pi}$.

Alternatively, we can use the raising and lowering operators.

Recall the position operator

$$\hat{x} = \sqrt{\frac{\hbar}{2mw}}(\hat{a}^\dagger + \hat{a})$$

where $\hat{a}^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$ is the raising operator and $\hat{a}\psi_n = \sqrt{n}\psi_{n-1}$ is the lowering operator. Now

$$E_0^{(1)} = H'_{00} = \left\langle \psi_0^{(0)} \middle| H' \middle| \psi_0^{(0)} \right\rangle = \left\langle \psi_0^{(0)} \middle| bx^4 \middle| \psi_0^{(0)} \right\rangle = b\left(\frac{\hbar}{2mw}\right)^2 \left\langle \psi_0^{(0)} \middle| (\hat{a}^\dagger + \hat{a})^4 \middle| \psi_0^{(0)} \right\rangle$$

$$= b\left(\frac{\hbar}{2mw}\right)^2 \left\langle \psi_0^{(0)} \middle| \hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a} + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} \right.$$
$$\left. + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}\hat{a} + \hat{a}\hat{a}^\dagger\hat{a}\hat{a} + \hat{a}\hat{a}\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}\hat{a}\hat{a} \middle| \psi_0^{(0)} \right\rangle$$

$$= b\left(\frac{\hbar}{2mw}\right)^2 \left\langle \psi_0^{(0)} \middle| \hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}\hat{a}^\dagger\hat{a}^\dagger + \hat{a}\hat{a}\hat{a}\hat{a}^\dagger \middle| \psi_0^{(0)} \right\rangle$$

$$= b\left(\frac{\hbar}{2mw}\right)^2 \left\langle \psi_0^{(0)} \middle| \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}\hat{a}^\dagger\hat{a}^\dagger \middle| \psi_0^{(0)} \right\rangle = b\left(\frac{\hbar}{2mw}\right)^2 \left(\sqrt{1}\sqrt{1}\sqrt{1}\sqrt{1} + \sqrt{1}\sqrt{2}\sqrt{2}\sqrt{1}\right) = 3b\left(\frac{\hbar}{2mw}\right)^2$$

Problem 2 Stark Effect - Perturbation of infinite square well with an external electric field.

Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to presence of an external electric field. Given a particle with charge q in an infinite square well $x \in \left[-\frac{a}{2}, \frac{a}{2}\right]$. It's Hamiltonian is thus $\hat{H}_0 = \dfrac{\hat{p}^2}{2m}$ (i.e. free particle in the interval) with potential

$$\boxed{V(x) = \begin{cases} 0 & \text{for } -\dfrac{a}{2} \le x \le \dfrac{a}{2} \\ \infty & \text{otherwise} \end{cases}}$$

Its energy eigenvalues are $E_n^{(0)} = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$ with energy eigenfunctions on the interval $x \in \left[-\frac{a}{2}, \frac{a}{2}\right]$

$$\boxed{\psi_n^{(0)}(x) = \begin{cases} \sqrt{\dfrac{2}{a}} \cos\left(\dfrac{n\pi}{a}x\right) & \text{for positive odd}\, n = 1, 3, 5, ... \\ \\ \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{n\pi}{a}x\right) & \text{for positive even}\, n = 2, 4, 6, ... \end{cases}}$$

The charged particle is subjected to a weak external electric field perturbation $\hat{H}' = qEx$ where E is a constant close to zero. The perturbed Hamiltonian is thus $\hat{H} = \hat{H}_0 + \hat{H}'$. The first order energy correction to the *nth* energy eigenvalue E_n is

$$\boxed{E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle = H'_{nn}} \tag{2.1}$$

where $\psi_n^{(0)}$ is the energy eigenstates for the unperturbed system, i.e. $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. Using equation (2.1) we have the first order energy correction to the ground state energy ($n = 1$) of the perturbed infinite square well

$$E_1^{(1)} = H'_{11} = \left\langle \psi_1^{(0)} \middle| H' \middle| \psi_1^{(0)} \right\rangle = \frac{2qE}{a} \int\limits_{-a/2}^{a/2} x \cos^2\left(\frac{\pi}{a}x\right) dx = 0$$

as the integrand $f(-x) = -x\cos^2\left(-\dfrac{\pi}{a}x\right) = -x\cos^2\left(\dfrac{\pi}{a}x\right) = -f(x)$ is an odd function. Recall also that the second order energy correction to the *nth* energy eigenvalue E_n is

$$\boxed{E_n^{(2)} = \sum_{k \ne n} \frac{\left| \left\langle \psi_k^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \ne n} \frac{|H'_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}} \tag{2.2}$$

Using equation (2.2) we have the second order energy correction to the ground state energy ($n = 1$) of the perturbed infinite square well

$$E_1^{(2)} = \sum_{k\neq 1} \frac{\left|\left\langle \psi_k^{(0)} \middle| H' \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_k^{(0)}} = \sum_{k\,\text{even}} \frac{\left|\left\langle \psi_k^{(0)} \middle| H' \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_k^{(0)}} + \sum_{k\,\text{odd}, k\neq 1} \frac{\left|\left\langle \psi_k^{(0)} \middle| H' \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_k^{(0)}}$$

$$= \sum_{k\,\text{even}} \frac{1}{\frac{\pi^2\hbar^2}{2ma^2} - \frac{k^2\pi^2\hbar^2}{2ma^2}} \left| \left(\frac{2qE}{a}\right)^2 \int_{-a/2}^{a/2} x \sin\left(\frac{k\pi}{a}x\right) \cos\left(\frac{\pi}{a}x\right) dx \right|^2$$

$$+ \sum_{k\,\text{odd}, k\neq 1} \frac{1}{\frac{\pi^2\hbar^2}{2ma^2} - \frac{k^2\pi^2\hbar^2}{2ma^2}} \left| \left(\frac{2qE}{a}\right)^2 \int_{-a/2}^{a/2} x \cos\left(\frac{k\pi}{a}x\right) \cos\left(\frac{\pi}{a}x\right) dx \right|^2$$

$$= \left(\frac{2qE}{a}\right)^2 \frac{2ma^2}{\pi^2\hbar^2} \left\{ \sum_{k\,\text{even}} \frac{1}{1-k^2} \left| \int_{-a/2}^{a/2} x \sin\left(\frac{k\pi}{a}x\right) \cos\left(\frac{\pi}{a}x\right) dx \right|^2 + \sum_{k\,\text{odd}\, k\neq 1} \frac{1}{1-k^2} \left| \int_{-a/2}^{a/2} x \cos\left(\frac{k\pi}{a}x\right) \cos\left(\frac{\pi}{a}x\right) dx \right|^2 \right\}$$

$$= 8m \left(\frac{qE}{\pi\hbar}\right)^2 \sum_{j=1}^{\infty} \left[\frac{1}{1-(2j)^2} \left| 2 \int_0^{a/2} x \sin\left(\frac{2j\pi}{a}x\right) \cos\left(\frac{\pi}{a}x\right) dx \right|^2 \right]$$

$$= 8m \left(\frac{qE}{\pi\hbar}\right)^2 \sum_{j=1}^{\infty} \left[\frac{1}{(1-2j)(1+2j)} \left| \int_0^{a/2} x \sin\left[(2j+1)\frac{\pi}{a}x\right] dx + \int_0^{a/2} x \sin\left[(2j-1)\frac{\pi}{a}x\right] dx \right|^2 \right]$$

$$= 8m \left(\frac{qE}{\pi\hbar}\right)^2 \sum_{j=1}^{\infty} \left[\frac{1}{(1-2j)(1+2j)} \right.$$

$$\left. \left| \frac{\sin\left[(2j+1)\frac{\pi}{2}\right] - \left[(2j+1)\frac{\pi}{2}\right]\cos\left[(2j+1)\frac{\pi}{2}\right]}{\left[(2j+1)\frac{\pi}{a}\right]^2} + \frac{\sin\left[(2j-1)\frac{\pi}{2}\right] - \left[(2j-1)\frac{\pi}{2}\right]\cos\left[(2j-1)\frac{\pi}{2}\right]}{\left[(2j-1)\frac{\pi}{a}\right]^2} \right|^2 \right]$$

$$= 8m \left(\frac{qE}{\pi\hbar}\right)^2 \sum_{j=1}^{\infty} \left[\frac{1}{(1-2j)(1+2j)} \left| \frac{(-1)^j}{\left[(2j+1)\frac{\pi}{a}\right]^2} - \frac{(-1)^j}{\left[(2j-1)\frac{\pi}{a}\right]^2} \right|^2 \right]$$

$$= -8m \left(\frac{qE}{\pi\hbar}\right)^2 \left(\frac{a}{\pi}\right)^4 \sum_{j=1}^{\infty} \left[\frac{1}{(2j-1)(2j+1)} \left(\frac{1}{[2j+1]^2} - \frac{1}{[2j-1]^2} \right)^2 \right]$$

$$= -\frac{512ma^4}{\pi^6} \left(\frac{qE}{\hbar}\right)^2 \sum_{j=1}^{\infty} \frac{j^2}{[(2j-1)(2j+1)]^5} = -\frac{512ma^4}{\pi^6} \left(\frac{qE}{\hbar}\right)^2 \frac{\pi^2(15-\pi^2)}{12288} = \boxed{-m\left(\frac{15-\pi^2}{24}\right)\left(\frac{a}{\pi}\right)^4\left(\frac{qE}{\hbar}\right)^2}$$

where in the above calculation, we have used the fact that

(i) $g(-x) = -x\sin\left(-\frac{k\pi}{a}x\right)\cos\left(-\frac{\pi}{a}x\right) = x\sin\left(\frac{k\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right) = g(x)$ is an even function.

(ii) $h(-x) = -x\cos\left(-\frac{k\pi}{a}x\right)\cos\left(-\frac{\pi}{a}x\right) = -x\cos\left(\frac{k\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right) = -h(x)$ is an odd function.

(iii) $2\sin\left(\frac{2j\pi}{a}x\right)\cos\left(\frac{\pi}{a}x\right) = \sin\left[(2j+1)\,\frac{\pi}{a}x\right] + \sin\left[(2j-1)\,\frac{\pi}{a}x\right]$ (factor formula)

(iv) $\int_0^{x_0} x\sin(nx)dx = \frac{\sin(nx_0) - nx_0\cos(nx_0)}{n^2}$ (Using integration by parts).

(v) $\sum_{j=1}^{\infty} \frac{j^2}{[(2j+1)(2j-1)]^5} = \frac{\pi^2(15-\pi^2)}{12288}$

Problem 3 Gaussian Perturbation of 1D linear harmonic oscillator.
Consider a one-dimensional linear harmonic oscillator perturbed by a Gaussian perturbation $\hat{H}' = \lambda e^{-ax^2}$. The perturbed Hamiltonian is thus

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}mw^2x^2 + \lambda e^{-ax^2} = \hat{H}_0 + \hat{H}'$$

where $\hat{H}_0 = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}mw^2x^2$ is the unperturbed Hamiltonian and $\hat{H}' = \lambda e^{-ax^2}$ is the perturbation. Recall the ground state energy eigenfunction of simple harmonic oscillator is $\psi_0^{(0)}(x) = \left(\dfrac{mw}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{mw}{2\hbar}x^2}$. Therefore the first order correction to the ground state energy is:

$$\begin{aligned} E_0^{(1)} = H'_{00} = \left\langle \psi_0^0 \middle| H' \middle| \psi_0^{(0)} \right\rangle = \left\langle \psi_0^{(0)} \middle| \lambda e^{-ax^2} \middle| \psi_0^{(0)} \right\rangle &= \lambda\sqrt{\frac{mw}{\pi\hbar}} \int_{-\infty}^{\infty} e^{-\left(a+\frac{mw}{\hbar}\right)x^2} dx \\ &= \lambda\sqrt{\frac{mw}{\pi\hbar}} \int_{-\infty}^{\infty} e^{-\left(\frac{a\hbar+mw}{\hbar}\right)x^2} dx = \lambda\sqrt{\frac{mw}{\pi\hbar}}\sqrt{\frac{\pi\hbar}{a\hbar+mw}} = \lambda\sqrt{\frac{mw}{mw+a\hbar}} \end{aligned}$$

where we have use the fact that $\displaystyle\int_{-\infty}^{\infty} e^{-kx^2} dx = \sqrt{\frac{\pi}{k}}$.

Problem 4 Perturbation of Coulomb's Potential. The perturbed Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

where the unperturbed Hamiltonian is the hydrogenic Hamiltonian $\hat{H}_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)\, r}$ and the perturbation is $\hat{H}' = V(r) - \left[-\frac{Ze^2}{(4\pi\varepsilon_0)\, r}\right]$ i.e. the difference between $V(r)$ and the Coulomb potential, where

$$V(r) = \begin{cases} \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\left(\frac{r^2}{R^2} - 3\right) & \text{for } r \le R \\ -\frac{Ze^2}{(4\pi\varepsilon_0)\, r} & \text{for } r > R \end{cases}$$

is the potential due to a nuclear charge that is distributed uniformly within a sphere of radius R. Since the electron is inside the atom ($r \le R$),

$$\hat{H}' = \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\left(\frac{r^2}{R^2} - 3\right) + \frac{Ze^2}{(4\pi\varepsilon_0)\, r} = \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\left(\frac{r^2}{R^2} - 3 + \frac{2R}{r}\right)$$

(a) The first order energy shift due to this perturbation is

$$\begin{aligned}
\Delta E = H'_{nlm,nlm} = E^{(1)}_{nlm} &= \left\langle \psi^{(0)}_{nlm} \middle| \hat{H}' \middle| \psi^{(0)}_{nlm} \right\rangle = \int \psi^*_{nlm} \hat{H}' \psi_{nlm} dV \\
&= \int_0^{2\pi}\int_0^{\pi}\int_0^{R} R^*_{nl}(r) Y^*_{lm}(\theta,\phi) \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) R_{nl}(r) Y_{lm}(\theta,\phi) r^2 \sin\theta dr d\theta d\phi \\
&= \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\int_0^R |R_{nl}(r)|^2 \left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr \int_0^{2\pi}\int_0^{\pi} |Y_{lm}(\theta,\phi)|^2 \sin\theta d\theta d\phi \\
&= \frac{Ze^2}{(4\pi\varepsilon_0)\, 2R}\int_0^R |R_{nl}(r)|^2 \left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr \quad \text{(shown)}
\end{aligned}$$

(b) Recall that the radial wave function is

$$R_{nl}(r) = -\sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-\rho/2} \rho^l L^{2l+1}_{n+l}(\rho) \tag{4.1}$$

(Equation 7.139a of Bransden and Joachain Page 360) where $\rho = \frac{2Z}{na_\mu} r$, $a_\mu = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}$ (Bohr radius), μ is the mass of the electron and

$$L^{2l+1}_{n+l}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!\,(2l+1+k)!} \frac{\rho^k}{k!} \tag{4.2}$$

(Equation 7.131 of Bransden and Joachain Page 359) is the *associated Laguerre polynomials*. For region inside the nucleus $l = 0$ (recall that l is already zero for ground state of hydrogen atom) and $r \simeq 0 \implies \rho \simeq 0$. Since ρ is small, we can ignore higher powers of ρ in equation 4.2 and let $k = 0$. Thus

$$L^1_n(\rho) = \sum_{k=0}^{n-1} (-1)^{k+1} \frac{(n!)^2}{(n-1-k)!\,(1+k)!} \frac{\rho^k}{k!} \simeq -\frac{(n!)^2}{(n-1)!} \tag{4.3}$$

where we have approximate equation (4.3) to the sum of the first term only since ρ is small. Substitute into the radial wave equation (4.1) we have

$$R_{nl}(r) \simeq -\sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-1)!}{2n(n!)^3}}\, L^1_n(\rho) \simeq \sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-1)!}{2n(n!)^3}}\, \frac{(n!)^2}{(n-1)!} \delta_{l0} = \left(\frac{2Z}{na_\mu}\right)^{\frac{3}{2}} \frac{\delta_{l0}}{\sqrt{2}}$$

where the kronecker delta $\delta_{l0} = \begin{cases} 1 & \text{if } l = 0 \\ 0 & \text{if } l \neq 0 \end{cases}$ is inserted to indicate the result is true only for $l = 0$.

As a result, the first order energy shift for region inside the nucleus is

$$\Delta E = \frac{Ze^2}{(4\pi\varepsilon_0)\,2R}\int_0^R |R_{nl}(r)|^2 \left(\frac{r^2}{R^2} + \frac{2R}{r} - 3\right) r^2 dr \simeq \frac{Ze^2}{(4\pi\varepsilon_0)\,2R}\left(\frac{2Z}{na_\mu}\right)^3 \frac{\delta_{l0}}{2}\int_0^R \left(\frac{r^4}{R^2} + 2Rr - 3r^2\right) dr$$

$$= \frac{e^2}{(4\pi\varepsilon_0)}\frac{Z^4}{a_\mu^3 n^3}\frac{2}{R}\left[\frac{r^5}{5R^2} + Rr^2 - r^3\right]_0^R \delta_{l0} = \frac{e^2}{(4\pi\varepsilon_0)}\frac{2}{5}R^2\frac{Z^4}{a_\mu^3 n^3}\delta_{l0} \quad \text{(shown)}$$

Problem 5 Perturbation of Hamiltonian in matrix form.

Given the Hamiltonian of a quantum mechanical system

$$\hat{H} = E_0 \begin{pmatrix} -5 & 3\varepsilon & 0 & 0 \\ 3\varepsilon & 5 & 0 & 0 \\ 0 & 0 & 8 & -\varepsilon \\ 0 & 0 & -\varepsilon & -8 \end{pmatrix} \quad \text{where } \varepsilon \text{ is small.}$$

Observe that $\hat{H}^\dagger = \hat{H} \Longrightarrow \hat{H}$ is Hermitian.

(a)

$$\hat{H} = E_0 \begin{pmatrix} -5 & 3\varepsilon & 0 & 0 \\ 3\varepsilon & 5 & 0 & 0 \\ 0 & 0 & 8 & -\varepsilon \\ 0 & 0 & -\varepsilon & -8 \end{pmatrix} = E_0 \left[\begin{pmatrix} -5 & 0 & 0 & 0 \\ 0 & 5 & 0 & 0 \\ 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & -8 \end{pmatrix} + \varepsilon \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \right] = \hat{H}_0 + \hat{H}'$$

where

$$\hat{H}_0 = E_0 \begin{pmatrix} -5 & 0 & 0 & 0 \\ 0 & 5 & 0 & 0 \\ 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & -8 \end{pmatrix} \quad \text{and} \quad \hat{H}' = \varepsilon E_0 \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

Since $\hat{H}_0$ is a diagonal matrix, its eigenvalues are $E_1^{(0)} = -5E_0, E_2^{(0)} = 5E_0, E_3^{(0)} = 8E_0, E_4^{(0)} = -8E_0$ with normalised eigenvectors

$$\left|\psi_1^{(0)}\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \left|\psi_2^{(0)}\right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad \left|\psi_3^{(0)}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \left|\psi_4^{(0)}\right\rangle \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad \text{respectively.}$$

The superscript (0) is to denote that these are energy eigenvalues and eigenvectors of unperturb state with $\varepsilon = 0$.

(b) Let $\hat{H} = E_0\hat{M}$ where $\hat{M} = \begin{pmatrix} -5 & 3\varepsilon & 0 & 0 \\ 3\varepsilon & 5 & 0 & 0 \\ 0 & 0 & 8 & -\varepsilon \\ 0 & 0 & -\varepsilon & -8 \end{pmatrix}$. We will find the eigenvalues and eigenvectors of $\hat{M}$.

The secular or characteristic equation:

$$0 = \det(\lambda I - M) = \begin{vmatrix} \lambda+5 & -3\varepsilon & 0 & 0 \\ -3\varepsilon & \lambda-5 & 0 & 0 \\ 0 & 0 & \lambda-8 & \varepsilon \\ 0 & 0 & \varepsilon & \lambda+8 \end{vmatrix}$$

$$= (\lambda+5) \begin{vmatrix} \lambda-5 & 0 & 0 \\ 0 & \lambda-8 & \varepsilon \\ 0 & \varepsilon & \lambda+8 \end{vmatrix} + 3\varepsilon \begin{vmatrix} -3\varepsilon & 0 & 0 \\ 0 & \lambda-8 & \varepsilon \\ 0 & \varepsilon & \lambda+8 \end{vmatrix}$$

$$= (\lambda+5) \left|\begin{matrix} \lambda-5 & 0 & 0 \\ 0 & \lambda-8 & \varepsilon \\ 0 & \varepsilon & \lambda+8 \end{matrix}\,\right|\begin{matrix} \lambda-5 & 0 \\ 0 & \lambda-8 \\ 0 & \varepsilon \end{matrix} \;\; + \;\; 3\varepsilon \left|\begin{matrix} -3\varepsilon & 0 & 0 \\ 0 & \lambda-8 & \varepsilon \\ 0 & \varepsilon & \lambda+8 \end{matrix}\,\right|\begin{matrix} -3\varepsilon & 0 \\ 0 & \lambda-8 \\ 0 & \varepsilon \end{matrix}$$

$$= (\lambda+5)\left[(\lambda-5)(\lambda-8)(\lambda+8) - \varepsilon^2(\lambda-5)\right] + 3\varepsilon\left[-3\varepsilon(\lambda-8)(\lambda+8) - \varepsilon^2(-3\varepsilon)\right]$$

$$= (\lambda+5)(\lambda-5)\left[(\lambda-8)(\lambda+8) - \varepsilon^2\right] - 9\varepsilon^2\left[(\lambda-8)(\lambda+8) - \varepsilon^2\right] = (\lambda^2 - \varepsilon^2 - 64)(\lambda^2 - 9\varepsilon^2 - 25)$$

$$\Longrightarrow \lambda = \pm\sqrt{64+\varepsilon^2} \text{ or } \pm\sqrt{25+9\varepsilon^2}$$

Hence the exact energy eigenvalues for $\hat{H}$ are $\boxed{\lambda_{3,4} = \pm E_0\sqrt{64+\varepsilon^2} \text{ and } \lambda_{2,1} = \pm E_0\sqrt{25+9\varepsilon^2}}$. Notice that all the eigenvalues are real numbers as $\hat{H}$ is Hermitian. In the above calculation, we have use the cofactor expansion along the first row to evaluate the 4×4 determinant and the Sarrus' rule to evaluate the 3×3 determinant. (Sarrus' rule only works for 3×3 determinant). Maclaurin expansion of λ's in ascending power of ε:

$$E_{3,4} = \lambda_{3,4} = \pm 8E_0 \left(1 + \frac{\varepsilon^2}{64}\right)^{\frac{1}{2}} = \pm 8E_0 \left(1 + \frac{\varepsilon^2}{128} + ...\right) \tag{5.1}$$

$$E_{2,1} = \lambda_{2,1} = \pm 5E_0 \left(1 + \frac{9\varepsilon^2}{25}\right)^{\frac{1}{2}} = \pm 5E_0 \left(1 + \frac{9\varepsilon^2}{50} + ...\right) \tag{5.2}$$

(c) First order energy correction to the energy eigenvalues:

$$\boxed{E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle = H'_{nn}} \tag{5.3}$$

"The first order correction to the energy is the expectation value of the perturbation, in the *unperturbed* state." Therefore

$$E_1^{(1)} = H'_{11} = \left\langle \psi_1^{(0)} \middle| H' \middle| \psi_1^{(0)} \right\rangle = \begin{pmatrix} 1 & 0 & 0 & 0 \end{pmatrix} \varepsilon E_0 \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 0$$

$$E_2^{(1)} = H'_{22} = \left\langle \psi_2^{(0)} \middle| H' \middle| \psi_2^{(0)} \right\rangle = \begin{pmatrix} 0 & 1 & 0 & 0 \end{pmatrix} \varepsilon E_0 \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 0$$

$$E_3^{(1)} = H'_{33} = \left\langle \psi_3^{(0)} \middle| H' \middle| \psi_3^{(0)} \right\rangle = \begin{pmatrix} 0 & 0 & 1 & 0 \end{pmatrix} \varepsilon E_0 \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = 0$$

$$E_4^{(1)} = H'_{44} = \left\langle \psi_4^{(0)} \middle| H' \middle| \psi_4^{(0)} \right\rangle = \begin{pmatrix} 0 & 0 & 0 & 1 \end{pmatrix} \varepsilon E_0 \begin{pmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 0$$

Hence there is no first order correction to the perturbed energy eigenvalues. Second order correction to the energy eigenvalues:

$$\boxed{E_n^{(2)} = \sum_{k \neq n} \frac{\left| \left\langle \psi_k^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{|H'_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}} \tag{5.4}$$

Applying the result (where $\psi_k^0 = \psi_k^{(0)}$ in the following expression):

$$E_1^{(2)} = \sum_{k \neq 1} \frac{\left|\langle \psi_k^0 | H' | \psi_1^0 \rangle\right|^2}{E_1^0 - E_k^0} = \frac{\left|\langle \psi_2^0 | H' | \psi_1^0 \rangle\right|^2}{E_1^0 - E_2^0} + \frac{\left|\langle \psi_3^0 | H' | \psi_1^0 \rangle\right|^2}{E_1^0 - E_3^0} + \frac{\left|\langle \psi_4^0 | H' | \psi_1^0 \rangle\right|^2}{E_1^0 - E_4^0} = \frac{|3\varepsilon E_0|^2}{-5E_0 - 5E_0} + 0 + 0 = -\frac{9}{10} E_0 \varepsilon^2$$

$$E_2^{(2)} = \sum_{k \neq 2} \frac{\left|\langle \psi_k^0 \,|\, H' \,|\, \psi_2^0 \rangle\right|^2}{E_2^0 - E_k^0} = \frac{\left|\langle \psi_1^0 | H' | \psi_2^0 \rangle\right|^2}{E_2^0 - E_1^0} + \frac{\left|\langle \psi_3^0 | H' | \psi_2^0 \rangle\right|^2}{E_2^0 - E_3^0} + \frac{\left|\langle \psi_4^0 | H' | \psi_2^0 \rangle\right|^2}{E_2^0 - E_4^0} = \frac{|3\varepsilon E_0|^2}{5E_0 + 5E_0} + 0 + 0 = \frac{9}{10} E_0 \varepsilon^2$$

$$E_3^{(2)} = \sum_{k \neq 3} \frac{\left|\langle \psi_k^0 \,|\, H' \,|\, \psi_3^0 \rangle\right|^2}{E_3^0 - E_k^0} = \frac{\left|\langle \psi_1^0 | H' | \psi_3^0 \rangle\right|^2}{E_3^0 - E_1^0} + \frac{\left|\langle \psi_2^0 | H' | \psi_3^0 \rangle\right|^2}{E_3^0 - E_2^0} + \frac{\left|\langle \psi_4^0 | H' | \psi_3^0 \rangle\right|^2}{E_3^0 - E_4^0} = 0 + 0 + \frac{|-\varepsilon E_0|^2}{8E_0 + 8E_0} = \frac{E_0}{16} \varepsilon^2$$

$$E_4^{(2)} = \sum_{k \neq 4} \frac{\left|\langle \psi_k^0 \,|\, H' \,|\, \psi_4^0 \rangle\right|^2}{E_4^0 - E_k^0} = \frac{\left|\langle \psi_1^0 | H' | \psi_4^0 \rangle\right|^2}{E_4^0 - E_1^0} + \frac{\left|\langle \psi_2^0 | H' | \psi_4^0 \rangle\right|^2}{E_4^0 - E_2^0} + \frac{\left|\langle \psi_3^0 | H' | \psi_4^0 \rangle\right|^2}{E_4^0 - E_3^0} = 0 + 0 + \frac{|-\varepsilon E_0|^2}{-8E_0 - 8E_0} = -\frac{E_0}{16} \varepsilon^2$$

Equation (5.1) and (5.2) gives the new perturbed energy eigenvalues as series expansion

$$E_1 = \lambda_1 = E_0 \left(-5 - \frac{9}{10}\varepsilon^2 + ... \right)$$

$$E_2 = \lambda_2 = E_0 \left(5 + \frac{9}{10}\varepsilon^2 + ... \right)$$

$$E_3 = \lambda_3 = E_0 \left(8 + \frac{1}{16}\varepsilon^2 + ... \right)$$

$$E_4 = \lambda_4 = E_0 \left(-8 - \frac{1}{16}\varepsilon^2 + ... \right)$$

(i) The ε^0 constant term gives the energy eigenvalues of the unperturbed system.

(ii) The ε term gives the first order correction to the perturbed energy eigenvalues. In this question, $E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| H' \middle| \psi_n^{(0)} \right\rangle = H'_{nn} = 0$ for all n as there is no ε term.

(iii) The ε^2 term gives the second order correction to the perturbed energy eigenvalues. In this question

$$E_1^{(2)} = -\frac{9}{10}E_0\varepsilon^2 \qquad E_2^{(2)} = \frac{9}{10}E_0\varepsilon^2 \qquad E_3^{(2)} = \frac{E_0}{16}\varepsilon^2 \qquad E_4^{(2)} = -\frac{E_0}{16}\varepsilon^2$$