1. **For the potential shown in the figure, find the approximate ground state energy upto the second order in V_0, assuming that $V_0 << \frac{\hbar^2\pi^2}{2mL^2}$.** **[5]**

   Here $H_0 = \frac{p^2}{2m}$ and $V(x) = V_0$ if $x \in [0, L/2]$ and is 0 otherwise.

   Unperturbed states is $\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ with energy $E_n^{(0)} = \frac{\hbar^2\pi^2 n^2}{2mL^2}$.

   The first order correction is given by

$$\begin{aligned} \langle \phi_1, V\phi_1 \rangle &= \frac{2V_0}{L} \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \\ &= \frac{1}{2} V_0 \end{aligned}$$

   For even n,

$$\begin{aligned} \langle \phi_1, V\phi_n \rangle &= \frac{2V_0}{L} \int_0^{L/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx \\ &= -2V_0 \frac{(-1)^{n/2}\, n}{\pi(-1+n^2)} \end{aligned}$$

   For odd n, $\langle \phi_1, V\phi_n \rangle = 0$.

   Hence the second order correction is

$$\begin{aligned} E_1^{(2)} &= \sum \frac{|V_{1n}|^2}{E_1^{(0)} - E_n^{(0)}} \\ &= -\frac{8V_0^2 mL^2}{\pi^4\hbar^2} \sum_{\text{even } n} \frac{n^2}{(n^2-1)^3} \\ &= -\frac{V_0^2 mL^2}{8\pi^2\hbar^2} \end{aligned}$$

   (The last step is not expected. $\sum\limits_{n=1}^{\infty} \frac{4n^2}{(4n^2-1)^3} = \frac{1}{64}\pi^2$)

2. **Consider a particle (mass m) moving in a perturbed 2D infinite well represented by a potential energy function**

$$U(x,y) = \begin{cases} \frac{\eta E_0}{L^2} xy & \text{if } x, y \in [0, L] \\ \infty & \text{Otherwise} \end{cases}$$

   where η is a small positive real number and $E_0 = \frac{\pi^2\hbar^2}{2mL^2}$. Find the first order correction to the first excited energy level (which is 2-fold degenerate). Also find the correction to the wave functions. **[5]**

   The first excited state is degenerate. Let $\psi_1 = \phi_{12}(x,y) = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$ and $\psi_2 = \phi_{21}(x,y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)$. Both have energy $\frac{5\hbar^2\pi^2}{2mL^2}$. Then

$$\begin{aligned} V_{11} &= \frac{4}{L^2}\frac{\eta E_0}{L^2} \int_0^L \int_0^L xy \sin^2\left(\frac{\pi x}{L}\right) \sin^2\left(\frac{2\pi y}{L}\right) dxdy \\ &= \frac{1}{4}\eta E_0 \end{aligned}$$

Also, $V_{22} = V_{11}$.

$$\begin{aligned} V_{12} &= \frac{4}{L^2}\frac{\eta E_0}{L^2}\left(\int_0^L x\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)dx\right)^2 \\ &= \frac{256}{81}\eta\frac{E_0}{\pi^4} \end{aligned}$$

Hence the matrix of the pertubation $\begin{bmatrix} \frac{1}{4}\eta E_0 & \frac{256}{81}\eta\frac{E_0}{\pi^4} \\ \frac{256}{81}\eta\frac{E_0}{\pi^4} & \frac{1}{4}\eta E_0 \end{bmatrix}$, And the eigenvalues are $\frac{\eta E_0}{209952\pi^8}\left(52488\pi^4 + 663552\right) = 2.8996\times10^{-3}\eta E_0$ and $\frac{\eta E_0}{209952\pi^8}\left(52488\pi^4 - 663552\right) = 2.2334\times10^{-3}\eta E_0$. The eigen vectors are $\frac{\psi_1\pm\psi_2}{\sqrt{2}}$.

3. **To obtain an estimate of the ground state of hydrogen atom, use the trial function $\phi(r) = \frac{1}{\alpha^2+r^2}$ (in atomic units).**

   (a) Show that $\langle\phi,\phi\rangle = \frac{\pi^2}{\alpha}$.

   (b) Show that $\frac{1}{2}\langle\phi,p^2\phi\rangle = \frac{\pi^2}{4\alpha^3}$.

   (c) Show that $\left\langle\phi,\frac{1}{r}\phi\right\rangle = \frac{2\pi}{\alpha^2}$.

   (d) Show that the energy estimate is -0.405 au.

[2+4+2+2]

$\phi(r) = \frac{1}{\alpha^2+r^2}$

The integrals in parts (a), (b) and (c) are simple and a substitution $r = \alpha\tan\theta$ will simplify these.

- $\langle\phi,\phi\rangle = \int_0^\infty (\phi(r))^2 4\pi r^2 dr = \frac{\pi^2}{\alpha}$
- $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{1}{a^2+r^2}\right)\right) = \frac{1}{r^2}\left(-6\frac{r^2}{(a^2+r^2)^2} + 8\frac{r^4}{(a^2+r^2)^3}\right)$
- $\frac{1}{2}\langle\phi,p^2\phi\rangle = -\frac{1}{2}\int_0^\infty \phi(r)\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\phi(r)\right)\right)4\pi r^2 dr = \frac{\pi^2}{4\alpha^3}$
- $\left\langle\phi,\frac{1}{r}\phi\right\rangle = \int_0^\infty \phi(r)\left(\frac{1}{r}\phi(r)\right)4\pi r^2 dr = \frac{2\pi}{\alpha^2}$
- $E = \frac{\alpha}{\pi^2}\left(\frac{\pi^2}{4\alpha^3} - \frac{2\pi}{\alpha^2}\right) = \frac{1}{4\alpha^2} - \frac{2}{\alpha\pi}$
- $\frac{d}{d\alpha}\left(\frac{1}{4\alpha^2} - \frac{2}{\alpha\pi}\right) = -\frac{1}{2\alpha^3} + \frac{2}{\alpha^2\pi}$
- $-\frac{1}{2\alpha^3} + \frac{2}{\alpha^2\pi} = 0 \Rightarrow \alpha = \frac{1}{4}\pi$
- Minimum $E = -0.405$ at $\alpha = \frac{\pi}{4}$

4. **Two electrons, moving in a common harmonic potential are described by a Hamiltonian**

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}m\omega^2\left(x_1^2 + x_2^2\right)$$

   in independent particle approximation. Sketch energy spectrum, separately for singlets ($S = 0$) and triplets ($S = 1$), showing atleast five levels. Write down the energy and the degeneracy of each level. [5]

5. **Show that the ground state energy of the helium atom, treating the electronic coulomb repulsion as perturbation, is $-Z^2 + \frac{5}{8}Z$. [5]**

Useful Information

$$\int_0^{\pi/2} \sin^n \theta \, d\theta = \frac{n-1}{n} \int_0^{\pi/2} \sin^{n-2} \theta \, d\theta$$

Figure for Problem 1