Problem Set 6

Variational Method and Perturbation Theory

1. Derive expressions for the energy through zeroth-, first-, and second-order in perturbation theory.

2. Apply the variational method to approximate solutions to the systems defined on the following page.

   (a) Report the energy of the lowest three states (the three smallest eigenvalues).

   (b) Graph $\Phi_1^*(x)\Phi_1(x)$, where $\Phi_1(x)$ is the eigenvector corresponding to the lowest energy state of the system.

   (c) Graph $\Phi_2^*(x)\Phi_2(x)$, where $\Phi_2(x)$ is the eigenvector corresponding to the second lowest energy state of the system.

   (d) Graph $\Phi_3^*(x)\Phi_3(x)$, where $\Phi_3(x)$ is the eigenvector corresponding to the third lowest energy state of the system.

3. Apply perturbation theory to each of the systems defined on the following page.

   (a) Approximate the energy of the lowest three states using zeroth-order perturbation theory.

   (b) Approximate the energy of the lowest three states using first-order perturbation theory.

   (c) Approximate the energy of the lowest three states using second-order perturbation theory.

Below, you will find particle in a box Hamiltonians with modified potentials. Note: All values are given in atomic units. α is given in Hartrees. The particle in the box is an electron ($m_{\mathrm{e}} = 1$).

1. Symmetric double-well potential

$$\hat{V} = V(x) = \begin{cases} 0 & \text{if } 0 \leq x < 4 \\ \alpha & \text{if } 4 \leq x \leq 6 \\ 0 & \text{if } 6 < x \leq 10 \\ \infty & \text{otherwise} \end{cases}$$

$$\alpha = 0.1,\ 1.0,\ 10.0$$

2. Asymmetric double-well potential

$$\hat{V} = V(x) = \begin{cases} 0 & \text{if } 0 \leq x < 4 \\ \alpha & \text{if } 4 \leq x \leq 6 \\ 0.5 & \text{if } 6 < x \leq 10 \\ \infty & \text{otherwise} \end{cases}$$

$$\alpha = 1.0,\ 2.0,\ 10.0$$

3. Finite square-well potential

$$\hat{V} = V(x) = \begin{cases} 0 & \text{if } 0 \leq x < 8 \\ -\alpha & \text{if } 8 \leq x \leq 12 \\ 0 & \text{if } 12 < x \leq 20 \\ \infty & \text{otherwise} \end{cases}$$

$$\alpha = 0.5,\ 2.0,\ 10.0$$

4. Linear potential

$$\hat{V} = V(x) = \begin{cases} \alpha x & \text{if } 0 \leq x \leq 10 \\ \infty & \text{otherwise} \end{cases}$$

$$\alpha = 0.1,\ 1.0,\ 10.0$$

5. Harmonic potential

$$\hat{V} = V(x) = \begin{cases} \alpha(x-5)^2 & \text{if } 0 \leq x \leq 10 \\ \infty & \text{otherwise} \end{cases}$$

$$\alpha = 0.5,\ 1.0,\ 2.0$$

Some Potentially Useful Equations

Energy eigenfunctions:	$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \; n = 1, 2, 3, \dots & \text{if } 0 \leq x \leq L \\ 0 & \text{otherwise} \end{cases}$
Energy eigenvalues:	$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \; n = 1, 2, 3, \dots$
Expectation value:	$\langle \hat{A} \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x)\hat{A}\Psi(x)\mathrm{d}x}{\int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)\mathrm{d}x}$
Kinetic energy operator:	$\hat{T} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$
Hamiltonian operator:	$\hat{H} = \hat{T} + \hat{V}$
Ket:	$\|n\rangle = \Psi_n(x)$
Bra:	$\langle n\| = \Psi_n^*(x)$
Bra-ket:	$\langle m\|\hat{A}\|n\rangle = \int_{-\infty}^{\infty} \Psi_m^*(x)\hat{A}\Psi_n(x)\mathrm{d}x$
Matrix form of an operator	$A_{mn} = \langle \Psi_m\|\hat{A}\|\Psi_n\rangle = \int_{-\infty}^{\infty} \Psi_m^*(x)\hat{A}\Psi_n(x)\mathrm{d}x$
Perturbation energy expansion	$\mathcal{E}_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$
Zeroth-order energy	$E_n^{(0)} = \langle \Phi_n^{(0)}\|\hat{H}_0\|\Phi_n^{(0)}\rangle$
First-order energy	$E_n^{(1)} = \langle \Phi_n^{(0)}\|\hat{H}_1\|\Phi_n^{(0)}\rangle$
Second-order energy	$E_n^{(2)} = \langle \Phi_n^{(0)}\|\hat{H}_1\|\Phi_n^{(1)}\rangle = \sum_{i,i\neq n} \frac{\langle \Phi_n^{(0)}\|\hat{H}_1\|\Phi_i^{(0)}\rangle\langle \Phi_i^{(0)}\|\hat{H}_1\|\Phi_n^{(0)}\rangle}{E_n^{(0)} - E_i^{(0)}}$
Variational theorem	$\mathcal{E}_0 \leq \frac{\langle \Phi\|\hat{H}\|\Phi\rangle}{\langle \Phi\|\Phi\rangle}$
Wavefunction expansion	$\Phi = c_1\phi_1(x) + c_2\phi_2(x) + \dots + c_n\phi_n(x)$
Optimization of coefficients	$\sum_n \langle \phi_m\|\hat{H}\|\phi_n\rangle c_n = E\, c_m$