

Homework assignment 1

Problem 1: Variational calculation

In this problem the energy and the ground as well as first excited state wave function of a particle in a box is estimated using the variational principle. While this problem can, of course, be solved exactly, it is instructive to see how well variational approach with rather simple trial functions can approximate the exact solutions.

The potential is:

$$V(x) = \begin{cases} 0 & -a \leq x \leq a \\ \infty & \text{elsewhere} \end{cases}$$

(a) Begin by approximating the ground state wave function in the interval $[-a, a]$ by the simplest even polynomial which goes to zero at $x = \pm a$ (thereby satisfying the boundary conditions):

$$\psi(x) = \begin{cases} a^2 - x^2 & \text{for } -a \leq x \leq a \\ 0 & \text{elsewhere} \end{cases}$$

(here the family of trial functions is reduced to a single trial function). Calculate the mean value of the Hamiltonian H in this state and compare it with the true ground state energy.

In parts (b) and (c), enlarge the family of trial functions by choosing an even fourth degree polynomial which goes to zero at $x = \pm a$:

$$\psi_\alpha(x) = \begin{cases} (a^2 - x^2)(a^2 - \alpha x^2) & \text{for } -a \leq x \leq a \\ 0 & \text{elsewhere} \end{cases}$$

(a variational family depending on the real parameter α).

(You can use mathematical handbooks or computer programs such as Matlab to determine the integrals, if you like).

(b) Show that the expectation value of H in the state $\psi_\alpha(x)$ is:

$$\langle H \rangle (\alpha) = \frac{\hbar^2}{2ma^2} \frac{33\alpha^2 - 42\alpha + 105}{2\alpha^2 - 12\alpha + 42}$$

and show that the values of α which minimize or maximize $\langle H \rangle (\alpha)$ are given by the roots of the equation:

$$13\alpha^2 - 98\alpha + 21 = 0 .$$

Show that one of the roots of this equation gives, when substituted into $\langle H \rangle(\alpha)$, a value of the ground state energy which is much more precise than the one obtained in part (a).

(c) What other eigenvalue is approximated when the second root of the equation obtained in part (b) is used to evaluate $\langle H \rangle$. Explain with reference to the general derivation of the variational principle. How good is this approximation?

(d) Write down an expression for a set of polynomial trial functions where the smallest root will give an estimate of the first excited state, i.e. an approximation to the ground state is avoided (use symmetry).

Problem 2: Perturbation theory

Consider a particle of mass m placed in an infinite two-dimensional well of width a :

$$V(x, y) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \text{ and } 0 \leq y \leq a \\ \infty & \text{elsewhere} \end{cases}$$

This particle is also subject to a perturbation W described by the potential:

$$W(x, y) = \begin{cases} w_0 & \text{for } 0 \leq x \leq a/2 \text{ and } 0 \leq y \leq a/2 \\ 0 & \text{elsewhere} \end{cases}$$

(a) Calculate the energy of the lowest energy level to first order in w_0 using perturbation theory.

(b) Calculate the change in the energy of the second lowest energy level as the perturbation W is applied (again using first order perturbation theory). Give an expression for the wavefunction of the system corresponding to the energy you calculate in terms of the zeroth order eigenfunctions.

(c) How much is the first excitation frequency changed when the perturbation W is turned on (to first order)?

Problem 3: Perturbation treatment of anharmonic oscillator

Consider the vibration of a diatomic molecule. The interaction potential $V(r)$ between the atoms has a minimum of $-\epsilon$ at r_m , $V(r_m) = -\epsilon$.

(a) Show that when deviations from $r = r_m$ are small enough so that terms on the order of $(r - r_m)^4$ can be neglected, the Hamiltonian describing the relative motion of the two atoms can be written as $H = H_0 + H'$, where $H_0 = -\epsilon + \frac{\hbar w}{2}(\hat{P}^2 + \hat{r}^2)$ with

$$\hat{r} \equiv \sqrt{\frac{\mu w}{\hbar}}(r - r_m), \quad w \equiv \sqrt{\frac{1}{\mu}V''(r_m)}, \quad \hat{P} \equiv i\sqrt{\frac{\hbar}{\mu w}}\frac{d}{dr}$$

and $H' = \sigma\hbar w\hat{r}^3$, μ is the reduced mass. Give an expression for σ in terms of known parameters, such as μ and w and a derivative of the potential.

(b) H_0 is the harmonic oscillator Hamiltonian with energy levels $E_n = (n + \frac{1}{2})\hbar w - \epsilon$ and eigenstates $|n\rangle$. H' is treated as a perturbation. Show that

$$H' = \frac{\sigma\hbar w}{\sqrt{8}} \left[a^{\dagger 3} + a^3 + 3Na^{\dagger} + 3(N+1)a \right]$$

where $a \equiv \frac{1}{\sqrt{2}}(\hat{r} + i\hat{P})$ and $a^{\dagger} \equiv \frac{1}{\sqrt{2}}(\hat{r} - i\hat{P})$ are the raising and lowering operators for the harmonic oscillator. They satisfy the following rules:

$$a^{\dagger}|n\rangle = \sqrt{n+1}|n+1\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle.$$

(c) Derive an expression for $\langle m|H'|n\rangle$. Show that the matrix elements are zero unless $m = n \pm 1$ or $m = n \pm 3$ and find the first order perturbation approximation to the energy levels.

(d) Derive an expression for the second order perturbation approximation to the energy levels.

(e) Assuming the electric dipole moment of the molecule changes linearly with the displacement $(r - r_m)$ of the nuclei from the equilibrium position, the probability of absorbing or emitting a photon (and therefore the intensity of spectral lines) is proportional to $\langle i|\hat{r}|f\rangle$ where i and f denote initial and final states. Show that the transition from ground state to second excited state is allowed when the perturbation H' is introduced to first order (i.e. evaluate the wave function to first order and show that the probability of absorbing a photon is non-zero) while the transition has zero probability when the interaction is purely harmonic.

Derive a second order perturbation approximation for the first overtone frequency (which corresponds to excitation from the ground state to the second excited state) in terms of the second and third derivative of the potential at $r = r_m$.