

HOMEWORK 2 The Variational Principle

Due: Monday February 9, 4:30 pm

Problem 1: Variational bound on the ground state in a power-like potential

Consider a particle of mass m moving in a one dimensional potential:

$$V(x) = \lambda x^4$$

We can obtain an upper bound on the energy of the ground state using the variational method. To find a trial wave function, we regard the potential $V(x)$ as a harmonic oscillator potential with a space-dependent frequency i.e. $V(x) = \frac{1}{2}m\omega^2(x)x^2$ with $\frac{1}{2}m\omega^2(x) = \lambda x^2$. This motivates us to choose the trial wave function to resemble the ground state of a harmonic oscillator potential:

$$\psi(x) = Ae^{-bx^2}$$

Normalizing this wave function gives us:

$$A = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}}$$

and the expectation value of the energy for this wavefunction is given by:

$$\begin{aligned} E(b) &= \langle \psi | H | \psi \rangle = A^2 \int_{-\infty}^{\infty} dx e^{-bx^2} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \lambda x^4 \right) e^{-bx^2} \\ &= \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} dx e^{-2bx^2} \left(\frac{\hbar^2}{2m} (2b - 4b^2 x^2) + \lambda x^4 \right) = \frac{\hbar^2 b}{2m} + \frac{3\lambda}{16b^2} \end{aligned}$$

Find the value of b which minimizes $\langle \psi | H | \psi \rangle$ and obtain an upper bound on the ground state energy.

Problem 2: The variational principle, orthogonality, and excited states

- a. Prove the following corollary to the variational principle. If $\langle \psi | \psi_g \rangle = 0$ then $\langle \psi | H | \psi \rangle \geq E_e$ where ψ_g is the ground state wave function, ψ is some trial wave function, and E_e is the first excited energy.

To do this, start by writing out ψ as an expansion of the energy eigenfunctions and then find the expectation value of H .

This may seem useless in practice since it is in general difficult to be sure if a state $|\psi\rangle$ is orthogonal to $|\psi_g\rangle$ when we don't know the ground state beforehand. However, given a potential $V(x)$ with some symmetry, it is often possible to say $\langle\psi|\psi_g\rangle=0$. For example, if the potential is an even function, then the ground state wave function should also be an even function. For a trial wave function that is an odd function, we know that it must therefore be orthogonal to the ground state wave function.

- b. Choose a set of trial wave functions (e.g. $|\Psi\rangle = Axe^{-bx^2}$, where A is an appropriate normalization factor to be computed in terms of b) defined by a single parameter b to obtain an upper bound on the first excited state energy of the one-dimensional harmonic oscillator, $V(x) = \frac{1}{2}m\omega^2(x)x^2$. Compare your answer with the exact solution for a harmonic oscillator.

Problem 3: Diatomic molecule

Consider a heteronuclear diatomic AB molecule with a basis set comprising of the atomic state $|A\rangle$ on atom A and the atomic state $|B\rangle$ on atom B. Let the Hamiltonian matrix elements be defined as follows

$$\langle A|H|A\rangle = 0 \quad \langle A|H|B\rangle = \beta \quad \langle B|H|B\rangle = 2\Delta$$

where β is negative and Δ is positive. The states A and B are normalized for simplicity.

- (a) For part (a) assume that the overlap $\langle A|B\rangle = \langle B|A\rangle = 0$. Show that the bonding and anti-bonding molecular states have the following energies

$$\text{Bonding state: } \Delta - (\Delta^2 + \beta^2)^{1/2}$$

$$\text{Anti-bonding state: } \Delta + (\Delta^2 + \beta^2)^{1/2}$$

Sketch your results on an energy level diagram, showing the levels of both atomic states and both molecular states.

- (b) For part (b) the overlap matrix elements are $\langle A|B\rangle = \langle B|A\rangle = S > 0$

Show that the energy of the bonding and anti-bonding molecular states are as follows

$$\text{Bonding state: } \frac{\Delta - \beta S - (\Delta^2 + \beta(\beta - 2S\Delta))^{1/2}}{1 - S^2}$$

$$\text{Antibonding state: } \frac{\Delta - \beta S + (\Delta^2 + \beta(\beta - 2S\Delta))^{1/2}}{1 - S^2}$$

If instead of working with the above atomic states $|A\rangle$ and $|B\rangle$, we worked with new states $|A'\rangle$ and $|B'\rangle$ such that

$$\langle A'|H|A'\rangle = \frac{-\beta S}{1-S^2} \quad \langle B'|H|B'\rangle = \frac{2\Delta - \beta S}{1-S^2}$$

$$\langle A'|H|B'\rangle = \langle B'|H|A'\rangle = \frac{(\beta(\beta - 2S\Delta))^{1/2}}{1-S^2}$$

and

$$\langle A'|A'\rangle = \langle B'|B'\rangle = 1 \quad \langle A'|B'\rangle = \langle B'|A'\rangle = 0$$

show that the same bonding and anti-bonding energy levels are obtained. How do you interpret this result.

Problem 4: The direct iteration method

The components of the Hamiltonian in a certain basis are given as:

$$H_{n,m}(\alpha) = \sin \left[\frac{(n+m)^{0.52}}{\ln(n+m+\alpha)} \right]$$

Where $1 \leq n, m \leq N_{\max}$ and $1 < \alpha < 2$ is a parameter. Do this problem in Matlab, C++, or any programming language. To compare or check your answers you may want to use an existent eigensolver (e.g. in MatLab). If you are using C++, you might want to use the [GSL Library](#).

1. Using $N_{\max} = 100$ and any allowable α , build the Hamiltonian.
2. Calculate the ground-state energy of the system using the direct iteration method.
3. Plot the error (a difference between the energy for a given iteration and the energy when the convergence has been reached) as a function of the iteration number.
4. Using the same method, find the energy of the first excited level.
5. Comment on the shape of the curve.

Hint: The direct iteration method

The direct iteration method is an iterative procedure in which you start with an arbitrary vector $\psi^{(0)}$, then you build up iterations as follow:

$$\psi^{(n)} = \frac{H\psi^{(n-1)}}{\|H\psi^{(n-1)}\|}$$

where $\|H\psi^{(n-1)}\|$ is the norm of the vector $H\psi^{(n-1)}$, and n is the iteration number.

The ground state energy is given by:

$$E[\psi^{(n)}] = \frac{\langle \psi^{(n)} | H | \psi^{(n)} \rangle}{\langle \psi^{(n)} | \psi^{(n)} \rangle}$$

The energy of the first excited level can be calculated in essentially the same manner, but taking into account an extra condition that the sought for solution should be orthogonal to the ground state.

The direct iteration method converges to either the lowest OR the highest eigenvalue (whichever has the greatest absolute value). We are interested in the lowest energy. In order to get the lowest eigenvalue we can do what is called “energy shifting.” To do this, subtract some constant value from every diagonal element of the Hamiltonian. (This value must not be too large so as to change the solution, and not so small so as to not force the problem away from the greatest eigenvalue and towards the smallest eigenvalue.)

Supplementary information on installing GSL and eigensolvers

Implementation of GSL on Windows

If you are using Dev-C++:

<http://www.quantcode.com/modules/smartfaq/faq.php?faqid=10>

If you are using the Microsoft C++ product:

<http://www.quantcode.com/modules/smartfaq/faq.php?faqid=33>

Solving Generalized Eigenvalue Problems

If you are using Matlab:

d = eig(A,B) returns a vector containing the generalized eigenvalues, if A and B are square matrices. For the generalized eigenvalue problem $Ax = \lambda Bx$

[V,D] = eig(A,B) produces a diagonal matrix D of generalized eigenvalues and a full matrix V whose columns are the corresponding eigenvectors so that $A*V = B*V*D$. More information can be found here: [link](#)

If you are using GSL:

In GSL generalized eigenvalue problems are formulated as: $\beta Ax = \alpha Bx$

Where the normal eigenvalues $\lambda = \alpha / \beta$

Implementation of the generalized eigenvalue solver is given by these functions:

http://www.gnu.org/software/gsl/manual/html_node/Real-Generalized-Nonsymmetric-Eigensystems.html

Keep in mind that your eigenvalue problem may include, real, symmetric, sparse, or hermitian matrices which may make your problem computationally easier by using some of these functions:

http://www.gnu.org/software/gsl/manual/html_node/Eigensystems.html