<div align="center">Computational Problem Set</div>

This problem set contains four "difficult" problems each of which will require you to write a computer program or use a symbolic manipulation package like Mathematica. You are required to do **one** of these problems. If you do more than one of these problems you will receive extra credit. You may work together with other people in the class but the aggregated groups must still turn in the answers to at least one different problem **per person**.

A complete solution to one of these problems will require that you submit:

1. computerized plots of the data (if a plot is required)

2. the source code to any program you wrote to solve the problem

3. the URL for a web page that outlines the steps you took to solve the problem and which provides links to the code and images of any plots you produced

If you are having trouble getting started on all of these, **please come talk to me**. These problems are **hard**, so don't leave them for the last minute!

1. Calculate and plot the transmission probability as a function of energy for the piecewise-flat M-shaped barrier shown in the picture below. You only need to do the range between 0 and V_0 (although going higher is also interesting). Specifically, consider the case where $V_0 = \frac{5h^2}{2ma^2}$ and where $b = 2a$ How do the energies of the tunnelling resonances relate to the
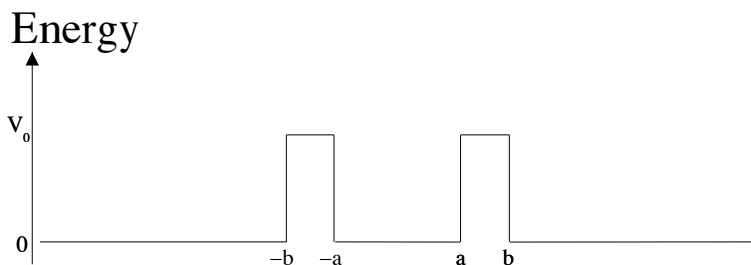
energies of a particle in a box with infinite walls at $-a$ and a? (Hint: Construct the boundary matching equations as a matrix problem

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{b}$$

where $\mathbf{x}$ is a vector of the amplitudes of the parts of the wavefunction, $\mathbf{b}$ is a vector containing only unit incoming flux, and the matrix $\mathbf{A}$ maps the coefficients in one region to the adjacent regions. Invert this equation (using Mathematica) to obtain the outgoing flux.)

Interpret your results!

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2. Consider a Harmonic oscillator that is in thermal contact with the rest of the universe, and which has come into thermal equilibrium. This is a magical harmonic oscillator which has only 6 energy eigenstates that may be populated. Those states are $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$, and $|5\rangle$

   (a) Compute the density matrix in the basis set of these six energy eigenstates.

   (b) Compute and plot $\langle x^2 \rangle$ as a function of temperature using this density matrix.

   (c) Plot $\langle x|\rho|x\rangle$ when $kT = 0.2\hbar\omega$, when $kT = \hbar\omega$, and when $kT = 5\hbar\omega$.

   Interpret your results!

3. One very common technique for obtaining eigenvalues and eigenvectors in linear algebra is *matrix diagonalization*. If we want to find the eigenvalues $\{\alpha_k\}$ and eigenfunctions $\{|k\rangle\}$ of any Hermitian operator $\hat{A}$,

$$\hat{A}|k\rangle = \alpha_k|k\rangle$$

we can formulate it as a matrix-diagonalization problem.

Here's how: If we choose a complete, orthonormal basis set $\{|n\rangle\}$ and expand the eigenfunctions as

$$|k\rangle = \sum_n |n\rangle\langle n|k\rangle = \sum_n c_n^{(k)}|n\rangle$$

then the eigenvalues of a *matrix* $\mathbf{A}$ whose elements are $[A]_{nn'} = \langle n|\hat{A}|n'\rangle$ are the same as the eigenvalues of *operator* $\hat{A}$, and the elements of the *eigenvectors* of $\mathbf{A}$ are just the coefficients for the *eigenfunctions* $\{|k\rangle\}$ in a basis set composed of the $|n\rangle$ functions.

That is, once we cast our operator in the form of a Matrix, we can use the tools from linear algebra to obtain the eigenvalues and eigenvectors. In this problem you will need to write a computer program to diagonalize a matrix and obtain the eigenvalues and eigenvectors. The problem centers on the energy levels of the Morse oscillator,

$$V(r) = D_e \left(1 - e^{-\beta(r-r_e)}\right).$$

This potential function has a Dissociation energy D_e, which is the difference between the minimum of the curve at r_e and the asymptotic energy at $r \to \infty$. In a previous problem set, you showed that

$$D_e\beta^2 = \frac{k}{2}$$

where k is the force constant of a Harmonic oscillator that closely matches the lower part of the curve,

$$V_{harmonic}(r) = \frac{k}{2}(r - r_e)^2 \tag{1}$$

The Morse oscillator is actually a solvable problem, and the exact energies are known (see Flüge's QM book or look in Karplus & Porter).

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What you will do in this problem is to pick the lowest 10 eigenstates $\{|n\rangle\}$ of the harmonic oscillator characterized by the potential in Eq. (1). Write the Hamiltonian for the Morse oscillator as a matrix in the basis set of Harmonic Oscillator states.

Construct a computer program that calculates the integrals for the matrix elements. Your program should also build a 10×10 Hamiltonian matrix for the Morse oscillator and diagonalize this matrix to give the eigenvalues. Compare your numerical eigenvalues to the exact eigenvalues.

4. In this problem, we will perform a real variational principle calculation to find the ground state energy of Helium using a set of Double-Zeta Slater-type Orbitals (STOs),

$$\phi_{1s_i} = \left(\frac{\zeta_i^3}{\pi}\right)^{1/2} e^{-\zeta_i r} = \sqrt{4\zeta_i^3} e^{-\zeta_i r} Y_0^0 \qquad i = 1, 2$$

as our trial functions. Here r refers to the radial coordinate between one of the electrons and the nucleus. To do this problem, you'll need to verify that the one electron integrals can be written:

$$S_{12} = \langle \phi_{1s_1} | \phi_{1s_2} \rangle = \frac{8\zeta_1^{3/2} \zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^3}$$

$$h_{12} = \langle \phi_{1s_1} | -\frac{\nabla^2}{2} - \frac{2}{r} | \phi_{1s_2} \rangle = \frac{4\zeta_1^{3/2} \zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^3} \left(2 - \frac{\zeta_1 \zeta_2}{\zeta_1 + \zeta_1}\right)$$

The *two* electron integrals are somewhat more difficult. To carry out these integrals you'll need the following identity:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2)$$

where $r_<$ means the smaller of r_1 and r_2 and $r_>$ means the larger.

In general, the two-electron integrals can be written:

$$(\mu\nu|\lambda\sigma) = \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \times$$

$$\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \phi_{1s_\mu}^*(\mathbf{r_1})\phi_{1s_\nu}^*(\mathbf{r_1})\frac{1}{r_{12}}\phi_{1s_\lambda}^*(\mathbf{r_2})\phi_{1s_\sigma}^*(\mathbf{r_2})$$

You may use the following derived expressions for the two-electron integrals (although you should verify at least one of them):

$$(11|11) = \frac{5}{8}\zeta_1$$

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$$(11|22) = \frac{\zeta_1^3\zeta_2(\zeta_1 + 4\zeta_2) + \zeta_1\zeta_2^3(\zeta_2 + 4\zeta_1)}{(\zeta_1 + \zeta_2)^4}$$

$$(12|12) = \frac{20\zeta_1^3\zeta_2^3}{(\zeta_1 + \zeta_2)^5}$$

$$(11|12) = \frac{16\zeta_1^{9/2}\zeta_2^{3/2}}{(3\zeta_1 + \zeta_2)^4}\left[\frac{12\zeta_1 + 8\zeta_2}{(\zeta_1 + \zeta_2)^2} + \frac{9\zeta_1 + \zeta_2}{2\zeta_1^2}\right]$$

Evaluate the integrals above together with h_{22}, h_{11}, $(22|21)$ and $(22|22)$ when $\zeta_1 = 1.45$ and $\zeta_2 = 2.91$.

Perform a variational calculation of the total energy of He$^+$ by using a double-zeta Slater basis function with these two values for ζ. The trial function is thus written as

$$\psi_{1s} = \sum_{i=1}^{2} c_i\phi_{1s_i}$$

where $\{\phi_{1s_1}, \phi_{1s_2}\}$ are the two Slater-type orbitals. Write a program that determines the minimum ground-state total energy obtained by varying c_1 and c_2. Comment on the discrepancy between the calculated and exact total energy.

Now, do the same for the Helium atom with both electrons.