

1. (a) Find the eigenfunctions and eigenvalues of the x component of the linear momentum operator.
 (b) Why must momentum eigenfunction always be complex?
 (c) According to the uncertainty principle, what is the uncertainty in the x position for a momentum eigenfunction?
 (d) given that for a particle in a square 1 dimensional infinite well that extends from $-a/2$ to $+a/2$, with the origin at $x=0$ (the center of the box), the lowest state wavefunction is $\cos(kx) = \frac{1}{2}[\exp(ikx) + \exp(-ikx)]$, one sometimes sees in textbooks ***“one will obtain only two possible momentum values when measuring the momentum of a particle in a square 1 dimensional infinite well”***. Is this statement correct, in your opinion?

Given what you learned in problem 1.(c) above about the extent of a momentum eigenfunction and the idea of writing the ground state of the particle-in-box as a linear combination of momentum eigenfunctions (a complete set), find a mathematical expression for the probability of measuring a value of p for this box.

2. Non-Linear Variation Method. For the Be^{+2} ion:

(a) Write down the Hamiltonian.

(b) Assume a trial wavefunction for the two electrons,

$$\Psi(\mathbf{1}, \mathbf{2}) = 1s(\mathbf{1})1s(\mathbf{2}) = \exp(-\alpha r_1) \exp(-\alpha r_2)$$

where α is an adjustable constant (sometimes called an “*effective nuclear charge*”). From information on this type of problem for the He atom, (the kinetic energy, $T = \alpha^2/2$ and potential energy $V = -\alpha Z + 5/8\alpha$ (in a.u.) for each orbital given in Lecture 7 on the website, find the value of α that gives the “best” wavefunction, and the energy given by this wavefunction.

(c) Verify that your answer obeys the virial theorem.

(d) Compare the answer to the exact answer given by that the sum of the *ionization energies of Be^{+2}* .

3. Linear Variation Method.

The purpose of this exercise, which might seem at first glance to be tedious, busy-work, is simply to reveal the several predictable invariant properties of the results of a linear variation calculation using 2 real, orthonormal basis functions. This amounts to valuable wisdom that will help you quickly see and understand” the physics underlying many quantum computations.

When the linear variation method is applied using as a trial wavefunction a linear combination of two orthonormal basis functions, Φ_1 and Φ_2 for the purpose of finding the lowest-energy linear combination,

$$\Psi_L = c_{1L} \Phi_1 + c_{2L} \Phi_2$$

the coefficients c_{1L} and c_{2L} (L stands for Lowest energy) come from solving the two simultaneous equations,

$$\begin{aligned} (H_{11} - E) c_1 + H_{12} c_2 &= 0 \\ H_{21} c_1 + (H_{22} - E) c_2 &= 0 \end{aligned}$$

where $H_{12} = \langle \Phi_1 | H | \Phi_2 \rangle$, the "interaction" of the two basis functions,

$H_{11} = \langle \Phi_1 | H | \Phi_1 \rangle$, the "energy" of Φ_1 ,

$H_{22} = \langle \Phi_2 | H | \Phi_2 \rangle$, the "energy" of Φ_2 ,

and $E = \langle \Psi | H | \Psi \rangle$. the expectation value of the energy using the **normalized** trial function.

For a non-trivial solution (c_1 and c_2 not both zero), the determinant of the matrix of numbers multiplying the coefficients c_1 and c_2 must vanish, i.e.,

$$(H_{11} - E)(H_{22} - E) - H_{21} H_{12} = 0$$

(a) For H_{12} real, **show** that the roots of the resulting quadratic equation may be rearranged to the easy-to-remember form:

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2}$$

Why is this "easier" to remember than the standard quadratic formula? Because it contains **only the physical quantities**: 1) the average energies of basis functions, 2) the median energy value of the basis functions, and 3) the interaction.

(b) What are the expressions for E , c_1 , and c_2 for two extreme cases of the following:

E_L , c_{1L} , and c_{2L} for the lowest energy and E_H , c_{1H} , and c_{2H} for the highest energy.
Assume $H_{11} < H_{22}$ and normalize ($c_1^2 + c_2^2 = 1$).

Case I: $H_{12} = 0$, $H_{11} < H_{22}$; Case II: $H_{11} = H_{22}$, $H_{12} < 0$.

Note: The above is equivalent to "diagonalizing" the H matrix ,
$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$$

i.e., finding the eigenvalues and eigenvectors:

$$H \begin{pmatrix} c_{1L} \\ c_{2L} \end{pmatrix} = E_L \begin{pmatrix} c_{1L} \\ c_{2L} \end{pmatrix} \quad \text{and} \quad H \begin{pmatrix} c_{1H} \\ c_{2H} \end{pmatrix} = E_H \begin{pmatrix} c_{1H} \\ c_{2H} \end{pmatrix}$$

(c) Demonstrate the following general facts concerning linear variation calculations for two orthogonal basis functions. Give at least **two** numerical examples for each case. To find the eigenvalues and

eigenvectors either use the equation in part 1 or use a computer program, e.g. from the internet: <http://www.colby.edu/chemistry/PChem/eigen.html>, or, <http://www.bluebit.gr/matrix-calculator/>, etc. (These two each have their strengths and weaknesses regarding input and output.)

- 1) ***One of the eigenvalues is always lower than the lowest diagonal element; the other is always higher than the highest diagonal element, no matter what the sign of the interaction (off-diagonal element). In other words, mixing always pushes the two states apart.***
- 2) ***If the interaction is negative, the lower-energy eigenvector coefficients are the same sign and those for the higher energy are opposite in sign. Vice versa if the interaction is positive.***
- 3) ***When the diagonal elements are equal (degenerate) the two basis functions are mixed equally, no matter what the interaction is (provided it is not zero) and the eigenvalues are equal to the diagonal element \pm the off diagonal element.***
- 4) ***If the energies of the basis functions (the diagonal elements) are not equal, the lowest-energy eigenvector will be mostly the lower-energy basis function and the higher energy eigenvector will be mostly the higher energy basis function.***
- 5) ***The farther apart in energy the two basis functions are, the less they mix (assuming a constant interaction).***
- 6) ***The larger the magnitude of the interaction, the more the mixing (assuming a constant diagonal energy difference).***
- 7) ***Adding a constant to both diagonal element shifts the eigenvalues by this constant and has no effect on the eigenvectors. (This is known as shifting the zero of energy.)***

8) **Perturbation limit for:**
$$\begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}$$

For the matrix above, where $\alpha_1 < \alpha_2$ and $\psi_1 = c_{11}\Phi_1 + c_{21}\Phi_2$, and $\psi_2 = c_{12}\Phi_1 + c_{22}\Phi_2$, show that when the interaction is small enough compared to the energy separation, the following perturbation formulas are valid.

$$E_1 = \alpha_1 - \frac{\beta^2}{\alpha_2 - \alpha_1}; \quad c_{11} \approx 1, \quad c_{21} \approx \frac{-\beta}{\alpha_2 - \alpha_1}$$

$$E_2 = \alpha_2 + \frac{\beta^2}{\alpha_2 - \alpha_1}; \quad c_{12} \approx \frac{\beta}{\alpha_2 - \alpha_1} \approx 1$$

This is perturbation theory. Test the formulas for values of $\beta/(\alpha_2 - \alpha_1) = 0.01, 0.1, 0.2, 0.5, 1$, and comment on their range of validity. That is, compare what these perturbation formulas give compared to the exact answer obtained by diagonalizing or the quadratic equation, and give your opinion concerning about what ratio of $\beta/(\alpha_2 - \alpha_1)$ is not giving a quality approximation.