

M. Sc. IV Semester 2019-20

Paper 4305- Advanced Quantum Mechanics

PARTICLE-IN-A-BOX

1. (a) Show that $\psi = A\exp(ikx) + B\exp(-ikx)$ is a solution to the particle in a one-dimensional box problem. Evaluate the constants A and B .

Is ψ an eigenfunction of \hat{p}_x ? Of \hat{p}_x^2 ?

What happens when \hat{p}_x operates on either half of ψ ? What does a solution in the form of ψ_2 imply about the measurement of p_x ?

(b) Re-evaluate A and B placing the origin at the middle of the box, i.e. $-\frac{L}{2} \leq x \leq \frac{L}{2}$.

Normalize the wave functions. Why are the wave functions different in this case? Would you expect any property: energies, probability density plots, expectation values of momentum, position to be different for this case? Which of these properties is different in this system? Would this affect σ_x ?

2. (a) (i) Show that the function $\psi = N \sin\left(\frac{n\pi x}{L}\right)$ satisfies the Schrödinger equation for a particle in a one-dimensional box with a potential function $V(x)$ equal to zero for $0 \leq x \leq L$ and infinity elsewhere.

(ii) What is the eigenvalue?

(iii) Describe what is meant by the *Born interpretation*, $P_n(x) = \psi_n^*(x)\psi_n(x)$?

(iv) What values may the quantum number n take? Sketch the first three wavefunctions and their probability density functions.

(v) Determine the average position and the average momentum of the particle for an arbitrary quantum state of the particle.

(vi) Show that the function is not an eigenfunction of the momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$ but it is so of \hat{p}^2 . Discuss the significance of the result.

(vii) What is the probability of finding the particle between $0.4L$ and $0.6L$ when (I) $n=1$, (II) $n=2$? What would you expect the answer to be for very large values of n ?

3. Using the fact that the half-wavelength of a single particle in a one-dimensional box must fit between the walls an integral number of times, and the de Broglie relationship $\lambda = h/p$, derive the equation $E = \frac{n^2 h^2}{8mL^2}$.

4. Each of the following particles is confined to a one-dimensional box. For each case calculate

- (a) the energy (in Joule) corresponding to the lowest energy level ($n = 1$);
- (b) the separation ($E_2 - E_1$) between the lowest and next-to-lowest energy levels;
- (c) the number of levels with energy less than the mean thermal energy $\frac{1}{2}kT$ at $T = 300$ K.

	Particle	Mass (m)	Length (L)
i)	Electron	9.11×10^{-31} kg	1 Å
ii)	H ₂ molecule	3.35×10^{-27} kg	1 cm
iii)	Ball	0.10 kg	1 m

5. In connection with the last question, estimate the quantum number corresponding to an energy kT at 300 K for each of the following. How close is the neighbouring level in each case?

- a) The mass is m_p , the mass of the proton (1.673×10^{-27} kg) and the box side is 5 Å.
- b) The mass is that of the proton, m_p , and the box is made much larger, to correspond to the volumes in which gases are customarily confined, for example, 0.1 m on a side.
- c) The mass is m_p and the box is made much smaller, to a length of 10^{-15} m, roughly the size of atomic nuclei.

The second of these will show very quickly how, in large containers, the quantization of energy levels is not observable because the levels are so closely spaced. Why do we neglect quantum effects in the Kinetic Theory of gases?

The third problem, the nuclear problem, will quickly give some feeling for why nuclear physics experiments require high-energy machines for the study of nuclear reactions, although one can use ordinary light to carry out chemical excitation processes.

6. Using your knowledge of the boundary conditions the wave functions must satisfy, explain what happens to the energy levels of a particle in a one-dimensional box if the box length is changed from L to L/k ($k = 2, 3, 4, \dots$).

7. Carbon nanotubes are thin hollow cylinders of carbon atoms that are excellent electrical conductors and can be used as wires in nanodevices. The tubes have diameters between 1 and 2 nm and lengths of several micrometres. A long carbon nanotube can be modelled as a one-dimensional structure. The electrons of the

nanotube are described by the wave function $\sin \pi x/L$, where L is the length of the nanotube.

- (a) Find the normalized wave function.
- (b) Compute the expectation value of the kinetic energy of the electron.
- (c) Compute the expectation value of the position of the electron.
- (d) Suppose the nanotube is of length $L = 10.0$ nm. Calculate the probability that the electron is
 - (i) between $x = 4.95$ nm and 5.05 nm,
 - (ii) between $x = 7.95$ nm and 9.05 nm,
 - (iii) between $x = 9.90$ nm and 10.00 nm,
 - (iv) in the left half of the box,
 - (v) In the central third of the box.

8. a) Show that the existence of zero-point energy is consistent with Heisenberg's Uncertainty Principle.

b) Calculate the zero-point energy for (i) a hydrogen atom confined to containers of length 1 nm, 100 nm, 1 cm; (ii) an electron in a piece of wire of length 1 cm, 0.1 nm.

c) Estimate the quantum number corresponding to an energy kT for a hydrogen molecule confined to a box of length 10 cm. How close is the neighbouring level?

Are your calculations consistent with the Correspondence Principle?

9. Define a reflection operator, \hat{R} , such that $\hat{R}\Psi(x) = \Psi(L-x)$ (if the origin is placed at $L/2$).

Show that the Hamiltonian for the particle in a one-dimensional box is invariant with respect to reflection, i.e. $\hat{R}\hat{H} = \hat{H}$. This implies that $[\hat{R}, \hat{H}] = 0$. Hence show that the eigenfunctions of the Hamiltonian operator are either symmetric or anti-symmetric with respect to reflection, provided they are non-degenerate.

10. Verify that the particle in a box wavefunctions form an orthonormal set.

11. For the states with $n = 1, 2, 3$, find the probability that the particle is in the region defined by (i) $0 \leq x \leq \frac{L}{2}$, (ii) $\frac{L}{3} \leq x \leq \frac{2L}{3}$.

12. Give a logical explanation for the fact that the kinetic energy increases as the number of nodes in the wave function increases.

13. a) For a particle in a one dimensional box whose probability distribution is given by the laws of classical mechanics, find $\langle x \rangle$ and $\langle x^2 \rangle$.

b) Compare with $\langle x \rangle$ and $\langle x^2 \rangle$ obtained from quantum mechanics. Show that the mean value of the position is at the centre of the well for all the quantum numbers.

For the $n = 2$ state, what is the probability of finding an electron in a small unit of length dx at this position? Can you rationalize the results?

c) Compare $\langle x^2 \rangle$ from (c) and (b) and show that this result is consistent with the Correspondence Principle.

d) Obtain $\langle p \rangle$ and $\langle p^2 \rangle$, and show that $\sigma_x \sigma_p \geq \frac{\hbar}{2}$.

(e) Calculate the minimum uncertainty in momentum and velocity of an electron in a 0.1 nm box, a hydrogen atom in a 1 nm box, and a 0.001 kg ball bearing in a 0.10 m box.

14. Show that the Hamiltonian operator for a particle constrained to move in a ring is $-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$, where $I = mr^2$, where r is the radius of the ring. Explain the significance of the quantities I and ϕ . What causes the energy to be quantized in this case? What is the lowest value that the quantum number n can have? Why is the lowest energy different for a particle in a ring and a particle in a box? Compare your solutions with those for the free unconstrained particle.

15. Assuming that the energies of the π electrons in a benzene ring are described by the "Particle on a ring" model, estimate the wavelength of the radiation needed to excite an electron from the highest occupied energy level to the lowest unoccupied energy level. Assume that each energy level can hold a maximum of two electrons, and that the radius of a benzene ring is 150 pm. The absorption spectrum of benzene contains a band at 260 nm. Compare your result with this value.

16. Show for the particle in a three-dimensional box, that $\psi(x, y, z)$ must be normalized within the limits ($0 \leq x \leq a, 0 \leq y \leq b, 0 \leq z \leq c$) of the box if each of the individual ϕ functions is normalized within their respective one-dimensional limits.

17. The term "state" and "energy level" are not synonymous in quantum mechanics.

For the particle in a cubic box, consider the energy range $E < \frac{15h^2}{8mL^2}$,

- How many states lie in this range?
- How many energy levels?
- Plot these levels on an energy scale and give their degeneracies.
- For a particle in a rectangular box of length L and width $L/2$, calculate the degeneracy of the level corresponding to $E = 20h^2/8mL^2$.

18. Consider a single particle of mass m in a cubic box of length L . Suppose that the system is perturbed slightly by pushing in one wall so that the new dimensions are $L \times L \times 0.99L$.

- Calculate the first seven energy levels, in units of $\frac{h^2}{8mL^2}$.

- b) Sketch an energy level diagram for the perturbed system indicating the degeneracy of each of the new levels.
 c) Given the results of (a) and (b), how would you expect the perturbation of any system to affect degeneracy?

19. Consider the case of a particle in a cubic box of length L . Suppose that the system is perturbed slightly by pushing in one wall so that the new dimensions are $L \times L \times (L - \lambda)$ where $\lambda \ll L$.

- a) Sketch an energy level diagram for the perturbed system (First show that

$$\Delta E_z = -\frac{n_z^2}{L^2} \left(1 + \frac{2\lambda}{L}\right) \text{ and take } \lambda \text{ as } 0.01.$$

- b) How would you expect the perturbation of any system to affect degeneracy?

20. Consider the particle in a three-dimensional box with $a = b = c/2$. What would be the energy when $n_x = 1, n_y = 2, n_z = 2$? For $n_x = 1, n_y = 1, n_z = 4$? Can you guess the meaning of the term “accidental degeneracy”?

For these two states (1,2,2) and (1,1,4), plot the nodal lines in the yz plane

21. Consider the problem of a particle in a cubic box of length L . If one side of the box is distorted by a small distance dx in one direction, the degeneracy of the first triply degenerate level is lifted. Calculate the difference between the resulting two sets of levels in Joule, if the particle has a mass 1.5×10^{-27} kg, the box of length 0.1 nm is distorted by 0.008 nm.

22. Derive the expression for the energies of the first excited state (2,1,1), (1,2,1) and (1,1,2) of a particle of mass m in a cubic box whose length has been elongated from L to $L + dL$ in one direction.

23. Show that the momentum of a wavefunction $\psi = e^{ikx}$ is $k\hbar$. Since

$$p_x = \sqrt{2mE} = \pm \frac{nh}{L} = k\hbar, \quad k = \pm \frac{2n\pi}{L}. \text{ Extending to the three dimensional case,}$$

$$k_x = \pm \frac{2n_x\pi}{L}, \quad k_y = \pm \frac{2n_y\pi}{L}, \quad k_z = \pm \frac{2n_z\pi}{L} \text{ and } k = \pm \frac{2\pi\sqrt{n_x^2 + n_y^2 + n_z^2}}{L}. \text{ Applying de}$$

Broglie's relation, $\lambda = \frac{h}{p} = \frac{h}{|\mathbf{k}|\hbar} = \frac{2\pi}{|\mathbf{k}|}$. This is the wavelength of the electron wave.

Notice that the quantum states with small amounts of momentum and energy have small values of $|\mathbf{k}|$. Thus in k -space they will be represented by points near the

origin. The equation $E = \frac{\hbar^2}{2m_e} [k_x^2 + k_y^2 + k_z^2]$ is the equation of a sphere. Thus, all

quantum states with energy E will be represented by points in k -space which lie on the

surface of a sphere with radius $|\mathbf{k}| = \sqrt{\frac{2m_e E}{\hbar^2}}$.

a) An electron occupies a quantum state with $k_x = 10^{-10} \text{ m}^{-1}$, $k_y = 10^{-10} \text{ m}^{-1}$ and $k_z = 0 \text{ m}^{-1}$. Work out the wavelength, energy, and speed of an electron occupying this state. (Ans. $\lambda = 4.44 \times 10^{-10} \text{ m}$; Energy = 7.58 eV; Speed = $1.633 \times 10^6 \text{ m/s}$).

b) Consider the case of a metal at the absolute zero of temperature, at which the N electrons in the metal occupy the N lowest energy quantum states. The region of occupied states forms an essentially perfect sphere, known as the *Fermi sphere*, with Fermi radius k_F . Since each electron occupies a ‘volume’ of k -space $4\pi^3/V$ (two electrons with up and down spins in the volume $(2\pi/L)^3$ in reciprocal space), we can

write $\frac{4}{3} \frac{\pi k_F^3}{4\pi^3} = N$ or $k_F^3 = 3 \left(\frac{N}{V} \right) \pi^2$ and $k_F = (3n\pi^2)^{1/3}$, where $n = N/V$ is the electron

density. We can also work out an expression for the energy (called the *Fermi energy*)

of electrons on the ‘surface’ of the Fermi sphere: $E_F = \frac{k_F^2 \hbar^2}{2m_e}$.

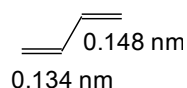
The density of copper (At. Wt. = 64.55 u) is $8.933 \times 10^3 \text{ kg m}^{-3}$. Assuming copper to be monovalent, estimate the number density, n , of ‘free electrons’ in copper. Also calculate the Fermi wave vector k_F and the Fermi energy for copper ($8.47 \times 10^{28} \text{ electron m}^{-3}$; $1.36 \times 10^{10} \text{ m}^{-1}$; 7.06 eV).

c) Sodium metal has the bcc structure (two atoms per unit cell) with a lattice constant of 0.422 nm. Calculate the Fermi energy (Ans. 3.2 eV).

The 3s band of solid Na will have as many orbitals (each delocalized over the entire solid) as the number of 3s orbitals from Na atoms in the sample. If each orbital of the sample can hold two spin-paired 3s valence electrons, to what extent will the band be filled? Hence, explain why sodium metal conducts electricity.

What about Mg? Explain why Mg conducts electricity though it has a completely filled 3s band. (The Fermi of Mg is 7.09 eV).

24. A useful first approximation to the optical properties of linear conjugated molecules may be obtained by considering the π -electrons as free electrons in a one-dimensional box with infinitely high walls. Consider butadiene



It has four π electrons that will fill the $n = 1$ and $n = 2$ levels of the ‘box’ (one π electron of each spin in each energy level). The first transition, which gives rise to an optical transition band, occurs when an electron jumps from the $n = 2$ level to the $n = 3$ level and the transition has a wavelength of 210 nm. To what length of box does the wavelength correspond?

How does this compare to the actual length of the conjugated system. β -carotene, one of the precursors of Vitamin A, has a conjugated system containing 11 double bonds

and a transition wavelength of 460 nm. Again compare the calculated and the actual length of the box (Bayliss, N. (1952) *Quart. Rev.* **6**: 319).

25. Because of delocalization, each of the six π electrons in the hexatriene molecule behaves approximately as if it were contained in a one-dimensional box whose length extends about one-half a bond length beyond each of the terminal carbons and is given as 0.73 nm.

- Calculate the first four energy levels for the π -electron in hexatriene.
- According to the Pauli exclusion principle, not more than two electrons may occupy a single energy level, so that six electrons completely fill the first three energy levels. What is the frequency and wavelength of the photon absorbed when a single electron undergoes a transition from the third to the fourth energy level? Compare this with the experimentally observed absorption band at 268 nm.
- Calculate the uncertainty in momentum for the electron in the $n = 3$ level of the hexatriene molecule.
- Calculate the expectation values of p_x , p_x^2 , and p_x^3 for the $n = 1$ level of the hexatriene molecule.
- For each of the three filled energy levels in hexatriene, compute the total particle density ($= 2\psi(x)^2$) since there are two electrons in each energy level at the points $x = L/8, L/4, L, 3L/8$ and $L/2$. Since all functions are symmetrical about $x = L/2$, the particle densities at $5L/8, 3L/4$ and $7L/8$ will also be known. Plot the particle densities as a function of x .

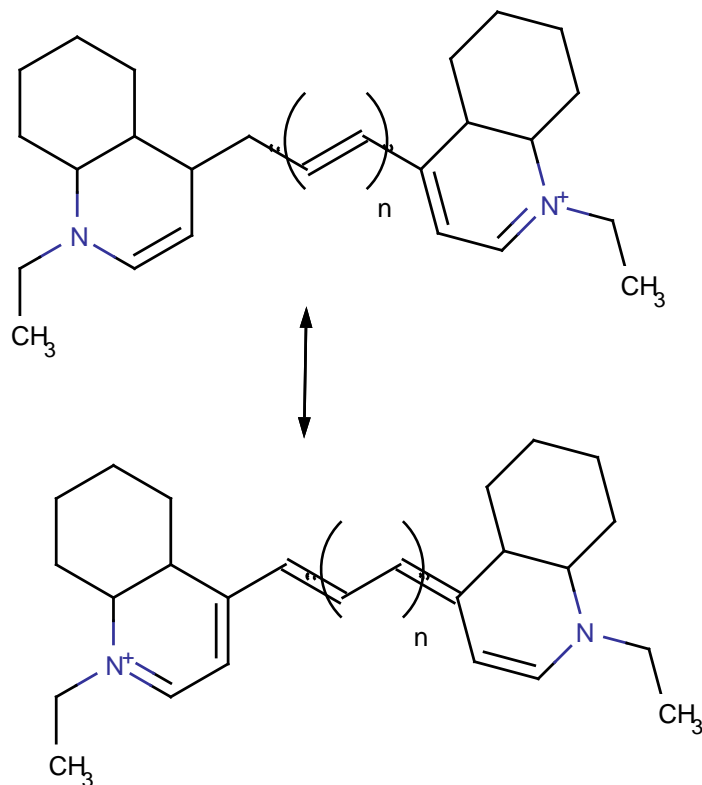
26. Now approximate the energy levels of hexatriene by using a one-dimensional box model whose length is the length of the molecule plus one C-C single bond length. Use 0.154 nm as a C-C and 0.135 nm as a C=C length. Using the six electrons to fill the three lowest energy levels, calculate the following quantities.

- The energy of the highest filled level.
- The energy of the lowest unfilled level.
- The difference in energy between the highest energy filled and the lowest energy unfilled levels. The energy difference should be approximately equal to the energy of the longest wavelength absorption band in the ultraviolet-visible spectrum of the dye. Compare your calculated energy with the experimental wavelength of maximum absorption $\lambda_{\max} = 268$ nm.
- Derive an expression for λ_{\max} for the general polyene $\text{H}_2-(\text{CH}=\text{CH})_n-\text{H}_2$.

Leave the length of the chain as an undetermined parameter in the expression for λ . (See Kuhn, H. *Helv. Chim. Acta* **31**: 1441 (1948); **34**: 1308 (1951); *J. Chem. Phys.* **29**: 1958 (1958) for help).

27. Kuhn (Kuhn, H. (1949) *J. Chem. Phys.* **17**: 1198) has suggested that the mobile π electrons in polymethine dyes can be modelled after the one-dimensional box. Consider the symmetric carbocyanine dyes (I) where the positive charge “resonates” between the two nitrogen atoms. The zigzag polymethines “path” along which the electrons are relatively free to move extends along the conjugated system between the two nitrogens. Kuhn assumed a bond length L equal to the path length plus one extra bond length on each end (so that the nitrogens would not be at the very edge of the

box where they would be prevented from having any π -electron charge). This gives $L = (2n + 10)l$ where $l = 0.139$ nm, the bond length of an intermediate (i.e. between single and double) C-C bond. The number of π electrons in the polymethine region is $2n + 10$. Assume that each energy level in the box is capable of holding no more than two electrons and that the electronic transition responsible for the dye colour corresponds to the promotion of an electron from the highest filled to the lowest empty level, the levels having initially being filled starting with the lowest, calculate ΔE and λ for the cases $n = 0, 1, 2, 3$, and compare with the observed λ values of maximum absorption of about 575, 715, 818, and 925 nm, respectively.



28. A very crude model of the buckminsterfullerene molecule (C_{60}) to treat it as a collection of electrons in a cube with sides of length equal to the mean diameter of the molecule 0.7 nm. Suppose that only the π electrons of the carbon atoms contribute. Calculate $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ and predict the wavelength of the first excitation of C_{60} to the $n + 1$ state. (The actual value is 730 nm.).

QUANTUM MECHANICAL TUNNELLING

1. a) Solve the problem of a particle in a one-dimensional box with one finite barrier at $x \leq 0$, and a finite barrier of $V = V_0$ at $x \geq L$. What are the boundary requirements responsible for quantization of energies in this case?
- b) Consider the effect of lowering the height of one wall of a one-dimensional box with infinitely high walls. Show that each energy level for a particle in the box will be lowered. Which levels are affected most and why? What does this imply about the involvement of core and valence electrons in chemical bonding?

c) Show that the transcendental equation for the energy levels lying lower than V_0 ($E < V_0$), is $\tan\left(\pm \frac{\sqrt{2mE}}{\hbar}\right) = -\sqrt{\frac{E}{V_0 - E}}$.

d) Show that the energies are continuous (not quantized) for the case $E > V_0$.

Plot the wave functions for both cases $E < V_0$ and $E > V_0$.

2. a) Show that for the particle in an infinite box with a finite central barrier

$$V = \begin{cases} \infty & |x| > L \\ V_0 & |x| < a \quad a < L \\ 0 & \text{otherwise} \end{cases}$$

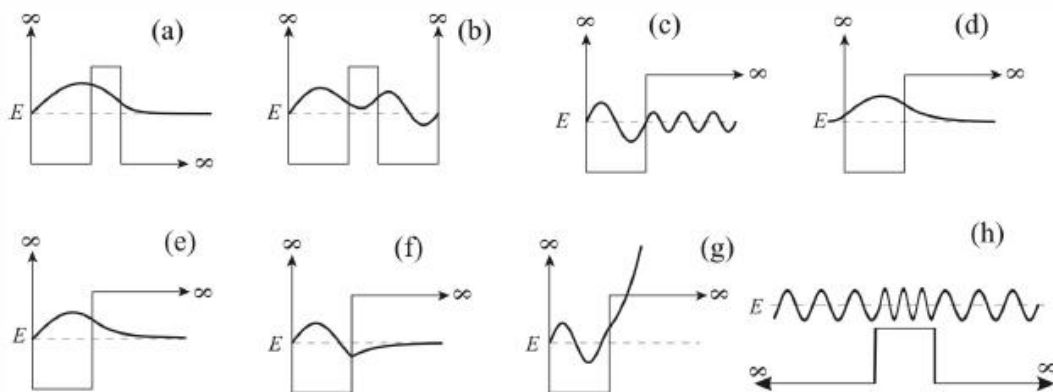
The wavefunctions must be either symmetric or antisymmetric with respect to reflection through $x = 0$ (the centre of the box).

b) Plot a correlation diagram relating energies when the central barrier is infinite (i.e. when the system is split into two infinite boxes) with those when the barrier vanishes. Hence, show that the lowest energy state for the system described in (a) must be symmetric, followed by an asymmetric level.

c) Plot the approximate wavefunctions for the case $E < V_0$ and $E > V_0$.

This kind of energy level plotting described in (b) is an extremely pervasive phenomenon in chemistry, e.g. in bond formation.

3. In a few words, indicate what is wrong with the wavefunctions sketched in the potentials shown below. In (h) the wave is incident from the left. If the solutions appear acceptable, indicate the fact.



4. (a) Explain how the phenomenon of quantum mechanical tunnelling has been exploited in the Scanning Tunnelling Microscope. How does the Atomic Force Microscope differ from the Scanning Tunnelling Microscope?

(b) The wavefunction of the electron in the gap between sample and needle in a Scanning Tunnelling Microscope is given by $\psi = Be^{-\kappa x}$ where $\kappa = \sqrt{2m_e(V - E)/\hbar^2}$. Assume that the tunnelling current is proportional to the transmission probability, which in turn is proportional to the square of the wavefunction. Sketch the tunnelling current versus tip to surface distance. If $V - E = 2.0$ eV, calculate by what factor the current would drop if the needle is moved from 0.50 nm to 0.60 nm from the surface?

(c) Why is it necessary to apply a bias voltage between the tip and surface in a scanning tunnelling microscope?

(d) Explain why tunnelling is more likely for a particle with $E = 3V_0/4$ than for $E = V_0/4$. What does this imply about the involvement of valence or core electrons in chemical bond formation?

HARMONIC OSCILLATOR

1. For a classical one-dimensional harmonic oscillator, show that the total energy $E = T + V = \frac{1}{2}kx_0^2$, where x_0 is the amplitude of the oscillator. Hence the system is conservative.

2. Consider a heteronuclear diatomic molecule lying along the x -axis, and let m_1 and m_2 be the masses of the two atoms, and x_1 and x_2 their respective displacements from their equilibrium positions.

a) Expand the potential energy for the system about the equilibrium interatomic distance R_e (i.e. about $x = 0$, where $x = x_2 - x_1$ is the net extension of the bond) and show that the potential energy function can be expressed in a parabolic form $\frac{1}{2}kx^2$ when x is small.

Write the expression for k and show that it is a positive quantity.

b) Obtain the kinetic energy and potential energy matrices, T and V , and find the generalized eigenvalues λ of the matrix V by solving the equation $(V - \lambda T)y = 0$. Obtain the eigenvectors y , too. Note that these are not orthogonal. To facilitate calculations, you need not normalize the eigenvectors. Show that the matrix of

eigenvectors is $G = \begin{pmatrix} 1 & m_2 \\ 1 & -m_1 \end{pmatrix}$ and the transformation that will diagonalize the two

matrices simultaneously is $G^{-1} = \begin{pmatrix} \frac{m_1}{M} & \frac{m_2}{M} \\ \frac{1}{M} & -\frac{1}{M} \end{pmatrix}$, where $M = m_1 + m_2$ is the mass of the

system.

Also show that, in terms of the new coordinates $q_1 = \frac{m_1x_1 + m_2x_2}{M}$ (centre of mass coordinates) and $q_2 = \frac{x_1 - x_2}{M}$ (internal coordinates), the two matrices are

$$V' = G^T V G = \begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{2} k M^2 \end{pmatrix} \quad \text{and} \quad T' = G^T T G = \begin{pmatrix} \frac{1}{2} M & 0 \\ 0 & \frac{1}{2} m_1 m_2 M \end{pmatrix} \quad \text{or} \quad V' = \frac{1}{2} k M^2 q^2$$

and $T' = \frac{1}{2} M \dot{q}^2 + \frac{1}{2} m_1 m_2 M \dot{q}_2^2$. To cast V' and T' in the more familiar forms, we let

$x = -\frac{q_2}{M} = x_2 - x_1$ and $x_m = q_1$. Hence $V' = \frac{1}{2} k x^2$ and $T' = \frac{1}{2} M \dot{x}_m^2 + \frac{1}{2} \mu \dot{x}^2$, where μ is the reduced mass. Hence, classically any two-body problem can be reduced to two simpler one-body problems by defining two sets of coordinates- centre of mass coordinates (which appear only in the kinetic energy part) and internal coordinates.

The two separated equations are

(i) $E_1 = \frac{1}{2} M \dot{x}_m^2$, which corresponds to the translational kinetic energy of a particle of mass M located at x_m . The corresponding quantum mechanical Schrödinger equation is $-\frac{\hbar^2}{2M} \frac{d^2 \psi_m}{dx_m^2} = E_m \psi_m$, which is the equation for a free particle and yields continuous energies.

(ii) The other equation is $E = \frac{1}{2} \mu \dot{x}^2 + \frac{1}{2} k x^2$, which is the energy of relative motion. The Schrödinger equation is $-\frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dx^2} + \frac{1}{2} k x^2 \psi = E \psi$, and should yield quantized energies. (Note: To separate translational energy of the molecule as a whole, replace the individual masses by the reduced mass μ and the coordinates by internal coordinates).

3. Show that the solution to the above equation is

$$\psi_n(\xi) = N_n H_n(\xi) e^{-\xi^2/2} \quad \text{or} \quad \psi_n(x) = N_n H_n(\sqrt{\beta}x) e^{-\beta x^2/2}$$

Where $\beta = \frac{\sqrt{\mu k}}{\hbar}$ and $H_n(\xi)$ are Hermite polynomials that obey Hermite's differential equation

$$H_n'' - 2\xi H_n' + 2n H_n = 0,$$

N_n is the normalization constant and $\xi = \sqrt{\beta}x$.

The Hermite polynomials are standardized by the condition that the coefficient of the highest power of ξ in $H_n(\xi)$ is $2n$. Verify that $G(\xi, t) = e^{-t^2+2\xi t} = \sum_{n=0}^{\infty} H_n(\xi) \frac{t^n}{n!}$ is a generating function for the Hermite polynomials (Hint: Note that $e^{-t^2+2\xi t} = e^{-(t-\xi)^2} e^{\xi^2}$ and expand both functions as Maclaurin series. Then show that $c_n = 2^n$ and the recursion formula for Hermite polynomials $\frac{c_{m+2,n}}{c_{m,n}} = \frac{2(m-n)}{(m+2)(m+1)}$ is obeyed.

Differentiate the generating function n times with respect to ξ to obtain Rodrigues formula

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} \left(e^{-\xi^2} \right)$$

Use this formula to obtain the normalization constant N_n for the n^{th} harmonic oscillator wavefunction.

4. a) Differentiate the generating function with respect to t and show that

$$H_1(\xi) = 2\xi H_0(\xi)$$

$$H_{n+2}(\xi) = 2\xi H_{n+1}(\xi) - 2(n+1)H_n(\xi) \quad (n \geq 0)$$

b) Differentiate the generating function with respect to ξ and show that

$$\frac{dH_{n+1}(\xi)}{d\xi} = (n+1)H_n(\xi) \quad (n \geq 0)$$

5. a) For the harmonic oscillator wavefunctions, obtain the following quantities $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p_x \rangle$ and $\langle p_x^2 \rangle$. You may need some of the recurrence relations (To obtain $\langle x^2 \rangle$, first find $\langle \xi^2 \rangle$. Then $\langle x^2 \rangle = \frac{\langle \xi^2 \rangle}{\beta}$).

Also show that $\sigma_x \sigma_p \geq \frac{\hbar}{2}$.

b) Use the expressions for $\langle p_x^2 \rangle$ and $\langle x^2 \rangle$ to show that, on the average, the harmonic oscillator stores half its energy as kinetic and half as potential energy.

6. a) Show that the harmonic oscillator wavefunctions are either symmetric or antisymmetric with respect to reflection through a plane passing through $x = 0$.

b) Show that the harmonic oscillator wavefunctions form an orthonormal set. (Note that this means that $N_m N_n \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_m(\xi) d\xi = \delta_{nm}$).

7. a) For what value of α is the function $\exp(-\alpha x^2)$ an eigenfunction of the Hamiltonian operator for the linear harmonic oscillator?

b) Give reasons why the following wavefunctions cannot be satisfactory wavefunctions for the harmonic oscillator:

i. $(2 - \xi - 3\xi^2) \exp(-\xi^2 / 2)$

ii. $2\xi \exp(\xi^2 / 2)$

8. (i) Find the expectation value of the position x and linear momentum p_x for the ground state of a simple harmonic oscillator. The ground state wavefunction has the form

$$\psi = \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\beta x^2 / 2}$$

(ii) Obtain the variance in momentum σ_p^2 for the ground state of the oscillator.

9. The Hamiltonian of an oscillator is given by $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 x^2}{2}$ where $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$.

Use the operators \hat{b}^+ and \hat{b}

$$\hat{b}^+ = \frac{1}{\sqrt{2m\hbar\omega}} [\hat{p} + i\omega m\hat{x}]$$

$$\hat{b} = \frac{1}{\sqrt{2m\hbar\omega}} [\hat{p} - i\omega m\hat{x}]$$

to estimate $\langle p^2 \rangle$ and $\langle x^2 \rangle$ for the n^{th} state (ψ_n).

10. The eigenfunctions for the harmonic oscillators are

$$\psi_n(x) = N_n H_n(\xi) e^{-\xi^2 / 2}$$

Where $N_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$, $\xi = \sqrt{\alpha} x$ and $\alpha = \frac{\sqrt{\mu k}}{\hbar}$

Show that $\psi_n(x)$ is normalized that $\langle p^2 \rangle$ (for $n = 1$ state) is given by

$$\langle p^2 \rangle = \frac{3}{2} \hbar \sqrt{\mu k}$$

11. a) Show that the amplitude of a quantum mechanical oscillator can exceed the classical value (classically $x_0 = \sqrt{\frac{2E}{k}}$). What is the significance of the result?

b) On a potential energy diagram, plot some of the energy states of a harmonic oscillator. Plot the wavefunctions on the same scale.

According to this model, how many lines will be observed in the IR (vibration) spectrum of a diatomic molecule, if only transitions with $\Delta n = \pm 1$ are allowed.

ANGULAR MOMENTUM AND HYDROGEN-LIKE IONS

1. (i) From the classical relation $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ for the angular momentum, \mathbf{L} , obtain expressions for the three components L_x , L_y and L_z in terms of the components of \mathbf{r} and \mathbf{p} .

(ii) Write down the quantum mechanical operators for the three components of the angular momentum in Cartesian coordinates.

(iii) Evaluate the commutators $[\hat{L}_y, \hat{L}_z]$ and $[\hat{L}^2, \hat{L}_z]$. What is the physical significance of the result?

2.(a) Show that the classical expression for the relative kinetic energy of a two dimensional rigid rotator is $E = \frac{L^2}{2I}$, where L is the angular momentum of the system, and I is the moment of inertia.

b) Express the Schrödinger equation for the system in spherical polar coordinates, and hence obtain an expression for \hat{L}^2 in spherical polar coordinates.

c) Separate the Θ and Φ parts, and show that $\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$ ($m = 0, \pm 1, \pm 2, \pm 3, \dots$).

d) Express \hat{L}_z in polar coordinates and hence show that these functions are eigenfunctions of the \hat{L}_z operator with eigenvalues $m\hbar$.

3. Show that the Θ equation is $\frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) + (\beta - \frac{m^2}{\sin^2 \theta})\Theta = 0$, where $\beta = 2IE/\hbar^2$. Substitute $z = \cos \theta$ and show that

$(1-z^2) \frac{d^2 P(z)}{dz^2} - 2z \frac{dP(z)}{dz} (\beta - \frac{m^2}{1-z^2}) P(z) = 0$, where $P(z) \equiv \Theta(\theta)$. For the case $m = 0$, this becomes Legendre's equation with $\beta = l(l+1)$, where l is a positive integer, and the solutions are Legendre polynomials, $P_l(x)$, $l = 0, 1, 2, \dots$

4. Since $\beta = l(l+1) = 2IE/\hbar^2$, the energies are quantized and $E = \frac{\hbar^2}{2I}l(l+1)$. In rotational spectroscopy, $\hbar^2/2I$ is called the rotational constant, B and the quantum number l is replaced by J .

Since $E = L^2/2I$, $\hat{L}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m}$, where l is a positive integer, and $\hat{L}_z Y_{l,m} = m\hbar Y_{l,m}$ where $m = 0, \pm 1, \pm 2, \dots, \pm l$. (This condition arises from the condition that solutions of the associated Legendre equation in Problem 2 be well-behaved). Hence there are $2l + 1$ states having the same l but different m quantum numbers.

The $Y_{l,m}$ are spherical harmonics and have the form

$$\left[\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}.$$

5. a) The step-up and step-down operators for angular momentum are defined as $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$ and $\hat{L}_- = \hat{L}_x - i\hat{L}_y$. Evaluate the following commutators $[\hat{L}^2, \hat{L}_+]$, $[\hat{L}^2, \hat{L}_-]$ and $[\hat{L}_z, \hat{L}_-]$.

b) Show that

$$(\hat{L}_x^2 + \hat{L}_y^2) Y_{l,m} = (l(l+1) - m^2) \hbar^2 Y_{l,m}$$

$$\hat{L}_- \hat{L}_+ Y_{l,m} = l(l+1) \hbar^2 Y_{l,m}$$

$$\hat{L}_z \hat{L}_+ Y_{l,m} = (m+1) \hbar Y_{l,m}.$$

What is the significance of these equations?

c) Also show that

$$\hat{L}^2 \hat{L}_- Y_{l,m} = l(l+1) \hbar^2 \hat{L}_- Y_{l,m}$$

$$\hat{L}_z \hat{L}_- Y_{l,m} = (m-1) \hbar \hat{L}_- Y_{l,m}$$

And $\hat{L}_{\pm} Y_{l,m} = \sqrt{l(l+1) - m(m \pm 1)} \hbar Y_{l,m \pm 1}$

d) Show that $\hat{L}_+ Y_{l,l} = 0$ and $\hat{L}_- Y_{l,-l} = 0$.

e) Show that $\hat{L}^2 = \hat{L}_- \hat{L}_+ + \hat{L}_z + \hat{L}_z^2$.

6. Show that, in central field problems (V function of r only), the following commutation rules hold:

$[\hat{H}, \hat{L}^2] = 0$, $[\hat{H}, \hat{L}_z] = 0$. What is the significance of these results?

7. (a) Express the Hamiltonian operator for hydrogen atom and hydrogen-like ions in atomic units. In the expression, μ is the reduced mass of the electron-nucleus pair. How does it compare with m_e , the mass of the electron?

b) For what value of α is the function $e^{-\alpha r}$ an eigenfunction of the Hamiltonian operator? What is the eigenvalue? Normalize this function.

c) Using this function, obtain the following: $\langle r \rangle$, $\langle r^2 \rangle$, $\left\langle \frac{1}{r} \right\rangle$ and the most probable value of r . Show that the average distance of the electron in the ground state of the hydrogen atom is 1.5 times the most probable distance. Justify the statement that “the hydrogen atom has a diameter of approximately one Å”.

d) Obtain $\langle T \rangle$ and $\langle V \rangle$ and show that $\langle E \rangle = -\langle T \rangle$, and hence $\langle V \rangle = 2\langle E \rangle = -2\langle T \rangle$. This is the *virial theorem*.

e) Calculate the probability that the electron is at a distance 2 a.u. from the nucleus.

f) Calculate the radius of the sphere that encloses a (i) 50%, (ii) 90 % probability of finding the hydrogen 1s electron.

g) Write down an expression for the radial distribution function $4\pi r^2 R_{n,l}^2$ and explain why this function has a different physical interpretation to $R_{n,l}^2$.

(h) For the 1s and 2s wavefunctions, plot $4\pi r^2 R_{n,l}^2 dr$ as a function of r . Also plot $R_{n,l}^2$ as a function of r . How many nodes are there in each of the two wavefunctions?

i) At classical turning points the kinetic energy vanishes and so the total energy is entirely potential energy. We can use this condition to get general expressions for the positions of the classical turning points.

Show that the inner and outer classical turning points for a hydrogen atom are given by the following expressions.

$$\left\{ \frac{n(n - \sqrt{n^2 - l(l+1)})}{2}, \frac{n(n + \sqrt{n^2 - l(l+1)})}{2} \right\}$$

Calculate the classical turning points for an electron in the hydrogen atom, with $l = 4$

and $n = 2, 3$, and 4.

Show that the inner forbidden region decreases in size and the start of the outer forbidden region occurs at larger distances with increasing n .

VARIATION THEOREM

1. a) Suppose that a particle is described by a state ψ which is not an eigenfunction of an operator \hat{A} . Show that the probability of observing a particular eigenvalue ' a_i ' of the operator \hat{A} in an experimental determination of the quantity associated with \hat{A} , is equal to the square of the Fourier coefficient in the expansion of ψ in terms of the eigenfunctions φ_i of \hat{A} ($\hat{A}\varphi_i = a_i\varphi_i$).

b) Let an approximate wavefunction for a particle in a box be given by $\psi(x) = Nx(L-x)$ ($0 \leq x \leq L$). Show that this is well-behaved function and normalize it. Expand this function in terms of the eigenfunctions of the particle in a box.

c) Calculate the average energy $\langle E \rangle$ using

- (i) the mean value theorem, and
- (ii) the Fourier expansion and compare with the exact ground state energy. What is the percentage difference? Comment on the magnitude of the energy ($\pi^2 = 9.87$).

d) Show that the probability that the particle is found in the ground state is 0.999. Why is the probability so high? Also show that the particle is found in a state with $n =$ even is zero. Explain this result in terms of the symmetry of the wavefunctions.

e) Use your results of parts (b) and (c) to state and prove the Variation Theorem.

2. In connection with the last problem, without doing actual calculations, answer the following:

a) What would be the approximate expectation value of the energy for a state described by $\psi = Nx\left(\frac{L}{2} - x\right)(L-x)$?

b) Which term in the Fourier expansion would make the maximum contribution and why? Can you predict whether any terms would be 'zero'?

Give reasons for your answers.

3. a) Can you use a trial function of the form $\psi'(x) = x(1+x^2)$ to estimate the ground state energy? Give reasons for your answer.

b) Variation method can be used to improve the ground state energy of the above problem with trial functions φ_1 and φ_2 , where $\varphi_1 = x(1-x)$ and $\varphi_2 = x^2(1-x)^2$. The two linear combinations obtained by the variation method correspond respectively to the energy values $9.8698 \frac{\hbar^2}{2m}$ and $102.1302 \frac{\hbar^2}{2m}$. Give reasons and indicate to which n values the two linear combinations correspond.

4. Using the variational principle, calculate the energy of the ground state of the particle in the box by taking the “true” wavefunction as the trial function and show that the result is $E = E_0 = \hbar^2/8mL^2$

5. If we use the normalized trial function $\psi = \sqrt{\frac{3}{L^3}}x$, $0 \leq x \leq L$ for the particle in a one-dimensional box, we find that the variational integral has the value zero which is less than the true ground state energy. What is wrong?

6. Using a trial function $Ce^{-\alpha x^2}$, calculate the ground state energy of an oscillator for which the Hamiltonian is $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$.

7. Use the trial function $\psi(r) = e^{-\alpha r}$, where α is a variational parameter, to determine the energy of the ground state of a hydrogen atom. The radial part of the Hamiltonian for the hydrogen atom has the form (in atomic units)

$$\hat{H} = -\frac{1}{2r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{1}{r}$$

List two other operators of which this trial wavefunction is an eigenfunction.

8. Let $\psi = N \exp(-\alpha r^2)$ be a trial function (not normalized) for the ground state of the hydrogen atom. Use the variation method to determine the minimum energy attainable from this form by variation of α . Find the average value of r and the most probable value of r for this wavefunction. Compare these r values and the average energy with the exact energy. Find the percentage error in energy.

9. (a) Schrödinger (1926) showed that the wavefunction or *orbital* for the hydrogen atom in its ground state can be written

$$\psi = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}$$

where r is the radial distance between the proton and the electron and ζ is the orbital exponent. Find the upper bound to the energy of the hydrogen atom by the variational method.

(b) Repeat using a Gaussian approximation to the wavefunction for the ground state of the hydrogen atom

$$\psi = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2}$$

Find the energy as a closed algebraic expression for the Gaussian trial function.

Show that, at the minimum energy, the minimization parameter $\alpha = \frac{8}{9\pi} = 0.283$. Use the variation method to determine the minimum energy attainable from this form by variation of α . Find the average value of r and the most probable value of r for this wavefunction. Compare these r values and the average energy with the exact energy. Find the percentage error in energy.

10. Use the trial function $\psi = ax(1-x) + bx^2(1-x)^2$ to determine the approximate ground state energy of a particle of mass m in a one-dimensional box of unit length.

11. (a) Use the trial function $\psi(r) = e^{-\alpha r}$, where α is a variational parameter, to determine the energy of the ground state of a hydrogen atom.

(b) What values of α and β would be obtained in a variational calculation on the hydrogen atom using a function $e^{-\alpha r - \beta r^2}$, where α and β are variation constants?

12. One of the many possible approximate wavefunctions for a helium atom contain an “effective” nuclear charge Z' as a variable parameter. This wavefunction gives rise to an energy $E = (Z')^2 - \frac{27}{8}Z'$ in a.u. Use the variation principle to compute the best possible energy obtainable with a wavefunction of this type.

PERTURBATION THEORY

1. (a) An electron (charge e) is confined to a cubic box of length L . The potential energy of the electron is given by

$$V(x, y, z) = 0 \quad \left\{ \begin{array}{l} 0 \leq x \leq L \\ 0 \leq y \leq L \\ 0 \leq z \leq L \end{array} \right.$$

$V = \infty$ elsewhere in space.

Find the first order correction to the first excited energy level (which is triply degenerate). If an electric field of strength ϵ is applied parallel to the z -axis (\perp to x and y). The perturbation may be taken as

$$\hat{H}' = \epsilon z$$

(b) Use perturbation theory to estimate the first order correction to the energy of the n^{th} state of a particle of mass m in a one-dimensional box of length L ($0 \leq x \leq L$), where the perturbation is of the form $H' = Vx/L$.

(c) Calculate the first order perturbation correction to the energy levels of a particle in a one-dimensional box when a constant electric field of strength F is applied. Take $\hat{H}' = eFx$.

2. Calculate the first order perturbation correction to the energy of a hydrogen-like ion by a perturbation of the form $\hat{H}' = Fz = Fr \cos \theta$ (in atomic units), where F is the strength of an electric field applied in the z direction.

MULTIELECTRON ATOMS

1. Besides the orbital angular momentum, there is a spin angular momentum. The corresponding operators are similar to the orbital angular momentum operators. Thus $[\hat{H}, \hat{S}^2] = [\hat{H}, \hat{S}_z] = 0$, $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$, $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ (in atomic units). There are two spin functions α and β which are orthonormal. Thus, $\int \alpha^2 d\sigma = \int \beta^2 d\sigma = 1$, $\int \alpha\beta d\sigma = 0$. For multi-electron atoms, $\hat{S}_z = \sum_i \hat{S}_{zi}$, $\hat{S}^2 = \left(\sum_i \hat{S}_i^2 \right)$, $\hat{S}_i = \sum_{-i} \hat{S}_{-i}$, etc.

For the helium atom, obtain zero-order functions, and use them to obtain an approximation to the ground state energy. Use perturbation theory and variation theorem to show that the best value of energy is obtained by using an exponent of 1.69 for the 1s orbital.

2. (a) Insert the Hamiltonian in au for He

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{r_{12}}$$

into

$$E = \iint dr_1 dr_2 \varphi^*(r_1)\varphi^*(r_2)\hat{H}\varphi(r_1)\varphi(r_2)$$

and show that

$$E = I_1 + I_2 + J_{12}$$

Where

$$I_j = \int dr_j \varphi^*(r_j) \left[-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j} \right] \varphi(r_j)$$

and

$$J_{12} = \iint dr_1 dr_2 \varphi^*(r_1)\varphi(r_1) \frac{1}{r_{12}} \varphi^*(r_2)\varphi(r_2)$$

Why is J_{12} called the Coulomb integral?

(b) Show that the energy of the 1s2s configuration of the He atom is $I_1 + I_2 + J_{12} \pm K_{12}$. Why is the triplet state lower in energy than the singlet?

3. Construct zero-order orthonormal wavefunctions for the 1s2s state for helium atom. Show that the antisymmetric space function is a triplet state and the symmetric space function is a singlet state. What are the term symbols for the two states? (Use $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$ operators to obtain the term symbols).

4. Show that the triplet state has an energy $E_T = E_0 + J - K$ and the singlet state has an energy $E_S = E_0 + J + K$. What is the meaning of the terms E_0, J and K in the above expressions?

What is the sign of the terms J and K ? Which is larger and why? On an energy level diagram, plot the energies of the (1s1s) and (1s2s) states, and indicate what splitting you would observe when a magnetic field is applied in the z -direction.

5. (a) Write down the Slater determinant for the ground state of the Helium atom. Explain how this determinantal wavefunction satisfies the Pauli Exclusion Principle.

(b) Justify the statement that the Coulomb integral

$$J_{12} = \iint 1s(1)2s(2) \frac{1}{r_{12}} 1s(1)2s(2) d\tau_1 d\tau_2 = \iint [1s(1)]^2 \frac{1}{r_{12}} [2s(2)]^2 d\tau_1 d\tau_2$$

for the 1s2s excited state of He is positive.

(c) Without invoking equations, explain why the energy of the triplet state is lower than that of the singlet state for He in the 1s2s configuration.

6. Show using an example that the following two formulations of the Pauli exclusion principle are equivalent:

- Wavefunctions describing a many-electron system must change sign under the exchange of any two electrons.
- No two electrons may have the same values for all four quantum numbers.

7. Outline the Hartree-Fock SCF procedure.

8. Write down the Slater determinant for the lithium atom.

CHEMICAL BONDING

1. Derive the secular equations for the trial wavefunction of the form

$$\psi = c_A \varphi_A + c_B \varphi_B$$

where the φ 's are the normalized atomic orbitals on atom A and B, and the c 's are the coefficients.

- (a) Write down the Hamiltonian and a trial wavefunction for the H_2^+ molecule ion.
- (b) Assuming that identical normalized hydrogen-like wavefunctions are chosen, show that the normalization constant is $(2+2S)^{-1/2}$, where S is the overlap integral.
- (c) Use the variation method to obtain the wavefunctions and the energies of the bonding and antibonding orbitals of the hydrogen molecule ion.
- (d) By expanding the probability density, $\psi^*\psi$, qualitatively confirm that $\psi_s = \sqrt{(2+2S)}(\varphi_A + \varphi_B)$ represents the wavefunction for a bonding orbital of H_2^+ .
- (e) Show that the energy of this orbital is

$$E = E_H + \frac{J + K}{1 + S} + \frac{1}{R_{AB}},$$

where R_{AB} is the internuclear distance.

- (f) Qualitatively demonstrate that $\psi_a = \sqrt{(2-2S)}(\varphi_A - \varphi_B)$ represents the antibonding orbital.

2. Show that $\psi = c_1 1s_A + c_2 2p_{zA}$ is normalized if $c_1^2 + c_2^2 = 1$.

3. (a) Write an LCAO-MO trial wavefunction for the H_2 molecule, assuming that identical normalized hydrogen-like wavefunctions are chosen. Show that the normalization constant is $(2+2S^2)^{-1/2}$, where S is the overlap integral.

(b) The trial Valence Bond wave function used by Heitler and London to describe the hydrogen molecule in terms of hydrogen-like wavefunctions is

$$\psi = c_1 \varphi_A(1) \varphi_B(2) + c_2 \varphi_A(2) \varphi_B(1)$$

Compare with the wavefunctions you wrote in (a) and comment on the missing terms.

4. φ_a and φ_b are chosen to be the normalized set of basis functions for a one-electron homonuclear diatomic system. It is found that the values for the integrals involving these functions are $H_{aa} = \int \varphi_a^* \hat{H} \varphi_a d\tau = -2$ a.u.; $H_{bb} = \int \varphi_b^* \hat{H} \varphi_b d\tau = -2$ a.u.; $H_{ab} = \int \varphi_a^* \hat{H} \varphi_b d\tau = -1$ a.u.; $S_{ab} = \int \varphi_a^* \varphi_b d\tau = 0.25$.

Find an upper bound for the exact lowest energy for this system. Find the corresponding LCAO *normalized* approximate wavefunction.

5. φ_a and φ_b are chosen to be the normalized basis functions for an LCAO wavefunction for a one-electron heteronuclear diatomic molecule. It is found that the values for some integrals involving these functions are $H_{aa} = \int \varphi_a^* \hat{H} \varphi_a d\tau = -2$ a.u.; $H_{bb} = \int \varphi_b^* \hat{H} \varphi_b d\tau = -1$ a.u.; $H_{ab} = \int \varphi_a^* \hat{H} \varphi_b d\tau = -0.5$ a.u.; $S_{ab} = \int \varphi_a^* \varphi_b d\tau = 1/3$,

where \hat{H} is the molecular Hamiltonian. Set up the secular determinantal equation and find the lowest electronic energy that can be computed from an LCAO wavefunction $c_a\phi_a + c_b\phi_b$. Find c_a such that $\langle E \rangle$ is minimized and the wavefunction is normalized (Ans. $\langle E \rangle$ (lowest) = -2.030 a.u., $\psi = 1.045\phi_a - 0.179\phi_b$).

6. For the lithium hydride (LiH) molecule: (a) Write the complete time-independent Schrödinger equation; (b) Write the electronic equation; (c) Write the nuclear wave equation.

7. Consider the one-electron molecule-ion HeH^{2+} : (a) Write down the Hamiltonian (Born-Oppenheimer approximation) for the electronic energy in atomic units for the system; (b) Calculate the electronic energies for the lowest energy state of this system in the separated atom and united atom limits. (Ans. Separated atoms: lowest energy for $\text{H}^+ + \text{He}^+(1s) = -2$ a.u.; For the united atom $\text{Li}^{2+}(1s) = -4.5$ a.u.).

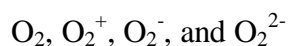
8. Draw and label an energy level diagram for molecular orbitals for a second row homonuclear molecule upto N_2 . Use the diagram to explain the following:

- (i) The bond length of Li_2 is much greater than that of B_2 .
- (ii) B_2 is paramagnetic but C_2 is not.
- (iii) NO^+ is more stable toward dissociation into its atoms than NO , whereas CO^+ is less stable than CO .
- (iv) He_2^+ ion in its electronic ground state is stable toward dissociation into He and He^+ .
- (v) The bond length in N_2^+ is 0.02 \AA greater than in N_2 , while the bond length in NO^+ is 0.09 \AA less than in NO .

9. (a) Predict the order of the N-O bond strengths in NO , NO^+ , and NO^- , and describe the magnetic properties of each. With what neutral homonuclear diatomic molecules are the NO^+ and NO^- ions isoelectronic?

(b) Compare the molecules OF , OF^- and OF^+ , discussing molecular orbitals, bond orders, bond lengths, bond energies, fundamental vibrational frequencies and paramagnetism.

(c) Arrange the following molecules in order of increasing bond length:



Which molecule will have the greater bond dissociation energy, O_2 or O_2^+ ?

(d) Compare the molecules OF , OF^- and OF^+ , discussing molecular orbitals, bond orders, bond lengths, bond energies, and paramagnetism.

10. Use sketches and symmetry arguments to decide which of the following integrals vanish for diatomic molecules: (a) $\int 1s_a 1s_b d\tau$; (b) $\int 2p_{za} 2p_{zb} d\tau$; (c) $\int 1s_a 2p_{zb} d\tau$; (d) $\int 2p_{xa} 2p_{zb} d\tau$; (e) $\int 1s_a 2p_{zb} d\tau$; (f) $\int 2p_{za} 2p_{yb} d\tau$

11. A homonuclear diatomic system has the ground state MO configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^2$.

(a) What is the net number of bonding electrons?

(b) Determine the states arising from this configuration and use Hund's rules to arrange them in order of increasing energy.

(c) What would you expect the effect to be on the dissociation energy of this molecule on ionization (i) from the $1\pi_g$ MO; (ii) from the $3\sigma_g$ MO?

(d) Upon ionization (one-electron) from the $1\pi_g$ level, what would be the spin multiplicity of the ground state?

12. Give the g and u character of the following types of molecular orbitals: (a) π^* in F_2 ; (b) σ^* in NO ?

13. Assign the 13 electrons in BO to appropriate bonding and antibonding orbitals. What is the bond order of the bond in BO ?

14. Give the MO configurations of the following species: H_2^- , N_2 , O_2 , CO , NO , CN .

13. Which of the following species: N_2 , NO , O_2 , C_2 , F_2 , CN would you expect to be stabilized (a) by the addition of an electron to form AB^- , (b) by ionization to AB^+ ?

15. Draw the MO diagram for (a) CO , (b) XeF , and use the Aufbau principle to put in the appropriate number of electrons. Is XeF^+ likely to be more stable than XeF ?

16. Write the valence-electron wavefunction for the HF molecule (regarding it as being formed from an H $1s$ -orbital and an F $2p_z$ orbital (a) supposing it to be purely covalent, (b) supposing it to be purely ionic, (c) supposing it to be 80 % covalent and 20% ionic.

17. Evaluate and graph the effects of dividing $H_{AA} \pm H_{AB}$ by $1 \pm S$ for each of the following cases: $H_{AA} = 0, -5, -10, -20$. In each case, let $H_{AB} = -5, S = 0.5$. Does the QMOT rule that antibonding interactions are more destabilizing than bonding interactions are stabilizing apply in all cases? Is the bonding level always the lower of the two? Does the QMOT expectation appear to be better followed by very low-energy levels, or by higher-energy levels?

18. Table 1 is a list of electron affinities (in eV) of certain molecules and atoms. Can you rationalize the molecular values relative to the atomic values using QMOT ideas?

Table 1 Atomic and Molecular Electron Affinities (in electron Volts)

H (0.75)	F (3.40)	N_2 (-1.6)
C (1.27)	H_2 (~ -2)	CO (< -1.8)

N (0.0±0.2)	C ₂ (3.5)	O ₂ (0.43)
O (1.46)	CN (3.82±0.02)	F ₂ (2.9)

19. a) Using the calculated molecular orbital energies shown in Table 2 for N₂ give the ionization energy when the electron is ionized from the highest-occupied orbital and when it is ionized from the second highest occupied orbital. The experimental results are 0.578 a.u. and 0.624 a.u., respectively.

Table 2 Molecular orbital energies (in a.u.)

N ₂	1σ _g	1σ _u [*]	2σ _g	2σ _u [*]	π _u	3σ _g [*]
	-15.722	-15.720	-11.952	-0.7396	-0.5795	-0.5445

b) Would the lowest energy transition of N₂ be a σ→π* or a π→π* type of transition?

20. (a) Explain the origin of the Lewis-base character of CO on the basis of MO theory.

(b) If CO were to lose its highest-energy electron (i.e. ionize), on which “end” of CO would most of the residual positive charge be found?

(c) Predict the “end” of the CO molecule that will be most positive in the ground state (after π→π*) be the same as in the ground state?

(d) Explain the formation of nickel-carbon monoxide complexes (Hint: Consider the bonding properties of both the lone pair and the availability of the ψ_{MO}^{π*} as a site for the d electrons of the nickel atom).

21. Which of the following species do you expect to be linear: H₂O, H₂O²⁺, H₂O⁺? Give reasons on the basis of both VB and MO theories.

22. For some time, it was uncertain whether the ground state of CH₂ and NH₂⁺ are singlets (2a₁)² or triplet (2a₁)(1b₁). The ground state geometries of these systems have HAH angles of 136° (CH₂) and 140-150° (NH₂⁺). Based on other data described in class for HAH systems, would you say these angles are more consistent with a singlet or a triplet ground state? Assuming that the first excited state is the other multiplicity, should the first excited state be more or less bent than the ground state?

23. Based on the Walsh diagram, what should happen to the geometry of H₂O upon 1b₁→3a₁ excitation?