Trial exam questions for Chemistry 356: Introduction to Quantum mechanics.

*In all cases indicate clearly how you get your answer. You only get partial credit for the correct result without explanation.*

*Carefully read the questions and verify you answer all parts of the question.*

*You have three hours to answer the questions (4 questions on the final).*

Table of Physical Constants:

\[
\begin{align*}
N &= 6.02 \times 10^{23} \\
e &= 1.602 \times 10^{-19} \text{ C} \\
h &= 6.63 \times 10^{-34} \text{ J sec} \\
c &= 2.998 \times 10^8 \text{ m/sec} \\
R &= 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J} \\
e &= 1.602 \times 10^{-19} \text{ J} = 8.066 \times 10^3 \text{ cm}^{-1} \\
a_0 &= 0.529 \text{ Å} = 0.529 \times 10^{-10} \text{ m} \\
a &= 9.11 \times 10^{-31} \text{ kg} \\
4\pi\varepsilon_0 &= 1.113 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \\
m_p &= m_n = 1.67 \times 10^{-27} \text{ kg} \\
k_B &= 1.381 \times 10^{-23} \text{ J K}^{-1}
\end{align*}
\]

**Atomic term symbol questions:**

1 a). Find the number of microstates in the (2p)^3 configuration of N and the resulting term symbols. Indicate the degeneracy of each term and use Hund's rules to order them according to increasing energy.

b). The sodium D line is the transition 3s → 3p. Find the term symbols for the ground and excited states. What is the degeneracy of each term? Indicating your reasoning, discuss why the D line is really two lines. Sodium vapor lamps use the yellowish 3p → 3s emission.
2. Consider the atom V (Vanadium) with 3 open-shell 3d electrons in the \([Ar]4s^23d^3\) configuration (assume that the 4s level is filled with two electrons). Determine the microstate of highest \(M_S\) with highest \(M_L\) value. Determine the corresponding \(S\) and \(L\) and the allowed \(J\) values and indicate the degeneracy and term value of each multiplet. Next consider the microstate with the highest possible \(M_L\) value of highest \(M_S\). Again determine the corresponding \(L\) and \(S\) and the allowed \(J\) values and indicate the degeneracy and term value of each multiplet you found. Make an energy plot to scale and order the states you found according to energy. Clearly indicate which energy levels are close in energy and which are more widely separated. How many microstates have you found in total? How many microstates are there in total in the \([Ar]4s^2d^3\) configuration?

3 a.) Find the number of microstates in the Carbon atom in its \(1s^22s^22p^2\) configuration and list the corresponding complete term symbols. Order these states according to energy following Hund's rules. Indicate which states lie very closely together in energy and which are further apart. The term symbols in the Oxygen atom are precisely the same as for the C atom. What is the energy ordering of the states in the O atom?

**Huckel Questions:**

4.

\[
\begin{align*}
\text{(I)} & \quad \text{HCCH} \\
\text{(II)} & \quad \text{H}_2\text{CCH}_2
\end{align*}
\]

a). Consider the \(\pi\) orbitals of the cyclopropenyl (I) and the allyl (II) radicals. Set up the Huckel determinant and determine the orbital energies of these two systems. The solutions for the first system are a little hard to find. Therefore it is sufficient to show that your polynomial equation can be written as \((x-1)^2(x+2) = 0\), from this you can easily find the roots by inspection. You should use these proper solutions for the rest of the
problem even if you did not derive them. Sketch the $\pi$ orbitals (use that they have to be symmetric or antisymmetric with reflection in the vertical axis through the middle of the molecule) for both cases and draw an orbital level diagram. What is the $\pi$-electron energy for the ground state of each of these systems and what is the spin state?

b). Next consider the anions (charge -1) and the cations (charge +1) for both of these systems. Indicate the orbital occupations in the ground state and specify the spin state for each of these four systems. Calculate the ionization energies ($E_{\text{cation}} - E_{\text{radical}}$) for both systems. Which system has the highest ionization energy?

5. Cyclobutadiene has four $\pi$-electrons and four sp$^2$ carbons.

We consider a square geometry in part (a) and a rectangle in part (b). Questions:

(a) For square C$_4$H$_4$, set up the Hückel determinant and sketch the $\pi$-MOs (indicating the phases) from the most bonding to most antibonding. Use orbitals that are either symmetric or asymmetric under reflection in the x- and y- axis (see figure). Show that the orbital energies $\alpha - 2\beta$, $\alpha$, and $\alpha + 2\beta$ are solutions to the Hückel problem. Make an orbital level diagram and show the MO occupations for the lowest triplet and the lowest singlet of the neutral molecule, and also for the ground state of the anion.

(b) Now consider rectangular C$_4$H$_4$ with bond lengths $a$ between C1-C2 and C3-C4 and bond length $b$ between C2-C3 and C1-C4. Consider the case $a < b$ and draw the orbital levels you expect now, also sketching the respective orbitals. Again show the MO occupations of the lowest triplet and singlet of the neutral molecule and the ground state of the anion. Do you expect the geometry of the singlet to be square or rectangular? What about the anion and the triplet state? Which state do you expect to differ most from a square? In all cases clearly indicate your reasoning.
Linear variational Problems (often a bit tedious)

Consider a modified harmonic oscillator Hamiltonian for \( m = k = 1 \) and including a linear perturbation. The total Hamiltonian is given by \( \hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2 + \frac{1}{5} x \), which we write as \( \hat{H} = \hat{H}_0 + \hat{V} \), where \( \hat{H}_0 = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2 \) and \( \hat{V} = \frac{1}{5} x \).

The two lowest normalized eigenfunctions \( \Psi_n(x) \) of \( \hat{H}_0 \) and the corresponding eigenvalues \( \varepsilon_n \) are given by

\[
\varepsilon_0 = \frac{1}{2}, \quad \Psi_0(x) = \left( \frac{1}{\pi} \right)^{\frac{1}{4}} e^{-\frac{1}{2} x^2}
\]

\[
\varepsilon_1 = \frac{3}{2}, \quad \Psi_1(x) = \left( \frac{4}{\pi} \right)^{\frac{1}{4}} x e^{-\frac{1}{2} x^2}
\]

We will use the trial function \( \Phi = c_0 \Psi_0(x) + c_1 \Psi_1(x) \) to approximate the eigenfunction of the full Hamiltonian. You are given the following integrals

\[
\begin{align*}
\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} \, dx &= \frac{1 \cdot 3 \cdot 5 \cdots (2n+1)}{2^n a^n (2n+1)} \left( \frac{\pi}{a} \right)^{\frac{1}{2}}, \quad n = 0, 1, 2, 3, \\
\int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} \, dx &= 0, \quad n = 0, 1, 2, 3, 
\end{align*}
\]

Questions:

a). Evaluate the matrix elements in the secular determinant of this 2x2 linear variational problem, making use of the fact that the \( \Psi_n(x) \) are orthonormal eigenfunctions of \( \hat{H}_0 \).

b). What are the corrections to \( \varepsilon_0 \) and \( \varepsilon_1 \) if you would use first order perturbation theory?

c). The exact eigenvalues of the Hamiltonian are given by \( E_0 = \varepsilon_0 - \frac{1}{50} \) and \( E_1 = \varepsilon_1 - \frac{1}{50} \).

Compare your variational results from a) with the exact results. Discuss that your results for the ground state are pretty good, but the excited state is not well described, and therefore the excitation energy \( E_1 - E_0 \) is not very good (calculate it). What is the excitation energy for your answer under b? What is the excitation energy if you would simply take \( \hat{H} = \hat{H}_0 \)? Compare with the exact result.
7. Consider the Hydrogen atom in its ground state in the presence of a magnetic field \( B \) in the \( x \)-direction. The full Hamiltonian is \( \hat{H}_0 + \gamma B \hat{S}_z = \hat{H}_0 + \frac{1}{2} \gamma B (\hat{S}_+ + \hat{S}_-) \), where \( \hat{H}_0 \) is the usual Hamiltonian, and assume \( \gamma B > 0 \). Take as your trial wavefunction

\[
\Psi = c_1 \alpha + c_2 \beta,
\]

where \( \hat{H}_0 \) is the usual Hamiltonian, and \( \alpha \) and \( \beta \) are the usual spin functions (eigenfunctions of \( \hat{S}_z \)). Set up the secular determinant for this problem. What are the two energies you find from the secular equations? What are the coefficients \( c_1 \) and \( c_2 \) for the ground state wave function? The energies you would find for a magnetic field pointing in the \( z \)-direction would be precisely the same. What is different in that problem?

**Angular momentum Theory. Often using \( J=\mathbf{L}+S \)**

8. The operator \( \hat{J} = \hat{L} + \hat{S} \) is an angular momentum operator with components

\[
\hat{J}_x = \hat{L}_x + \hat{S}_x, \quad \hat{J}_y = \hat{L}_y + \hat{S}_y, \quad \hat{J}_z = \hat{L}_z + \hat{S}_z
\]

that satisfy the general commutation relations for angular momentum operators (listed on the next page for your convenience). In addition

\[
[\hat{L}_i, \hat{S}_j] = [\hat{L}^2, \hat{S}_j] = [\hat{S}^2, \hat{L}_j] = 0 \quad \forall i, j = x, y, z, +, -
\]

You are asked to prove a number of identities below making use of (4.1) and the general relations. You are advised to use the results listed in previous parts of the question to prove the subsequent parts of the question. If you are stuck in the middle, you can go on with the next part, simply using the information from the previous part of the question (without proof).

Demonstrate the following:

a. \( [\hat{J}_z, \hat{L}^2] = 0 \) (so you can use also \( [\hat{J}_x, \hat{L}^2] = [\hat{J}_y, \hat{L}^2] = 0 \))

b. \( [J_z^2, \hat{L}^2] = 0 \) (hence it follows \( [\hat{J}_z, \hat{L}^2] = 0 \). No proof required)

c. \( \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2(\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z) \)

d. \( \hat{L}_x \hat{S}_- + \hat{L}_- \hat{S}_x = 2(\hat{L}_x \hat{S}_z + \hat{L}_z \hat{S}_x) \)

e. \( \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + \hat{L}_x \hat{S}_+ + \hat{L}_+ \hat{S}_x + 2\hat{L}_z \hat{S}_z \) (use the information from c. and d.)

f. \( [\hat{S}_z, \hat{J}^2] = \hbar \hat{L}_z \hat{S}_+ - \hbar \hat{L}_+ \hat{S}_z \) (use form of \( \hat{J}^2 \) from e.)
General relations on angular momentum theory for your perusal:

A general vector-operator $\hat{K}$ with components $\hat{K}_x, \hat{K}_y, \hat{K}_z$, $\hat{K}^2 = \hat{K}_x^2 + \hat{K}_y^2 + \hat{K}_z^2$ is said to be an angular momentum operator if it satisfies the commutation relations

$$[\hat{K}_x, \hat{K}_y] = i\hbar \hat{K}_z; \quad [\hat{K}_z, \hat{K}_x] = i\hbar \hat{K}_y; \quad [\hat{K}_y, \hat{K}_z] = i\hbar \hat{K}_x \tag{A.1}$$

In such a case we can define

$$\hat{K}_+ = \hat{K}_x + i\hat{K}_y; \quad \hat{K}_- = \hat{K}_x - i\hat{K}_y \tag{A.2}$$

and write

$$\hat{K}^2 = \hat{K}_+ \hat{K}_- + \hat{K}_z^2 - \hbar \hat{K}_z \tag{A.3}$$

$$[\hat{K}_z, \hat{K}_+] = \hbar \hat{K}_z; \quad [\hat{K}_z, \hat{K}_-] = -\hbar \hat{K}_z \tag{A.4}$$

We also know that

$$[\hat{K}^2, \hat{K}_x] = [\hat{K}^2, \hat{K}_y] = [\hat{K}_z, \hat{K}_+] = [\hat{K}^2, \hat{K}_+] = [\hat{K}^2, \hat{K}_-] = 0 \tag{A.5}$$

For your information: This question (in addition to some further parts) can be used to show that $\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z$ all commute, and hence they have common eigenfunctions. This is the reason we can label atomic eigenfunctions by quantum numbers $L, S, J, M_J$.

However, $\hat{S}_z$ and $\hat{L}_z$ do not commute with $\hat{J}^2$ (see part f), and $M_S$ and $M_L$ are not good quantum numbers. Indeed we do not use them in the atomic term symbols. We only use them to find the possible $L$ and $S$ (highest $M_S$ and $M_L$).

9. The function $\alpha \sin \theta e^{i\phi}$ is an eigenfunction of both the $\hat{J}^2$ and $\hat{J}_z$ operators, where $\hat{J} = \hat{L} + \hat{S}$ is the operator for total angular momentum. Here $\alpha$ is the spin “up” function, while $\beta$ indicates the spin down function. Below you will be asked to construct other eigenfunctions of this operator. I will first provide some definitions that you will need. We will use atomic units for convenience, so $\hbar = 1$.

$$\hat{J}_+ = \hat{L}_+ + \hat{S}_+, \hat{J}_- = \hat{L}_- + \hat{S}_-, \hat{J}_z = \hat{L}_z + \hat{S}_z$$

$$\hat{J}^2 = \hat{J} \cdot \hat{J}_+ + \hat{J}_-^2 + \hat{J}_z^2$$
\[ \hat{L}_z = -i \frac{\partial}{\partial \varphi} \]
\[ \hat{L}_+ = e^{i\varphi}[\frac{\partial}{\partial \theta} + i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \varphi}] \]
\[ \hat{L}_- = e^{-i\varphi}[\frac{\partial}{\partial \theta} - i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \varphi}] \]
\[ \hat{S}_\alpha = 0; \hat{S}_\beta = \beta; \hat{S}_+ \beta = \alpha; \hat{S}_- \beta = 0; \hat{S}_z \alpha = \frac{1}{2} \alpha; \hat{S}_z \beta = -\frac{1}{2} \beta \]

Please remember that \( \hat{S}_k \) does not act on functions of \( \theta, \varphi \), while \( \hat{L}_k \) does not act on the spin functions (they are like constants). Questions:

a). Show that \( \psi = \alpha \sin \varphi \) is an eigenfunction of \( \hat{J}_z \). What is the corresponding eigenvalue?

b). Show that \( \hat{J}_+ \psi = 0 \) and use this to show that \( \psi \) is an eigenfunction of \( \hat{J}^2 \). What is the corresponding eigenvalue?

c). Act with the ladder operator \( \hat{J}_- \) on \( \psi \) and continue this process of acting with \( \hat{J}_- \) to generate the set of functions that are all eigenfunctions of \( \hat{J}^2 \) with the same eigenvalue. For each function indicate the eigenvalue of \( \hat{J}_z \).

d). Show that \( \hat{J}_- \beta \sin \varphi e^{-i\varphi} = 0 \). Show also that this function is an eigenfunction of \( \hat{J}_z \). What is the corresponding eigenvalue?

10. (Electron spin resonance) The magnetic part of the Hamiltonian for an H atom (S = 1/2, I = 1/2) in the ground state in a magnetic field \( B \) in the \( z \) direction is given by

\[ \hat{H} = -g_e \mu_e B \hat{S}_z - g_N \mu_N B \hat{I}_z + A \hat{S} \cdot \hat{I} \]

where the \( \hat{S} \) operator acts on the electronic spin coordinate while the \( \hat{I} \) operator refers to the proton. The \( \hat{S} \cdot \hat{I} \) terms represents a coupling between the electron and nuclear magnetic moments. In this problem indicate the spin up and spin down functions for the electron as \( \alpha_e, \beta_e \) while the nuclear spin functions are indicated by \( \alpha_p, \beta_p \). Let me note that

\[ g_e \mu_e >> g_N \mu_N. \]

a. For \( A = 0 \), write down the spin eigenfunctions, their energies, and order them with increasing energy. Indicate with arrows which transition(s) correspond to flipping only the electron spin \( S \) but not the nuclear spin and find the transition energy. What is the degeneracy of this transition?
b. Before we will consider the case $A \neq 0$ show the operator identity
\[ \hat{S} \cdot \hat{I} = \frac{1}{2}(\hat{S}_z \hat{I}_z + \hat{S}_+ \hat{I}_+) + \hat{S}_- \hat{I}_-, \]
using that $\hat{S}$ and $\hat{I}$ are general angular momentum operators.

c. Now assume $A > 0$ and use first-order perturbation theory to find the energy shifts of the levels obtained under a). Make use of the info gained under b) to simplify your calculation. Again indicate the transitions that correspond to flipping purely the electron spin. How many transitions do you predict? What is the splitting between the transitions? This phenomenon is called hyperfine interaction and it is a major source of information in electron spin resonance spectroscopy.

**Variational problems with a parameter.**

11. Consider the following trial wavefunction:
\[ \Psi(x) = \begin{cases} 
N(x^3 - A^2 x) = Nx(x - A)(x + A), & -A \leq x \leq A \\
0, & x < -A \text{ or } x > A 
\end{cases} \]
for the Harmonic oscillator Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$. $N$ in the above is the normalization constant, while $A$ is the variational parameter, to be determined. First sketch the wave function for the value $N=A=1$. Clearly show if the function is even or odd with respect to reflection in $x=0$. Calculate the energy $E$ as a function of $A$ for a normalized wave function, and optimize the parameter $A$, using the variational principle. You will find (if everything is done correctly) that your energy is greater than
\[ E_i = \frac{3}{2} \frac{\hbar}{\sqrt{k/m}}. \]
Please reason carefully that the trial wave function is orthogonal to the exact ground state (for any value of $A$), and explain that therefore the trial energy $E(A) \geq E_i$. You have found an approximation for the first excited state.

12. Consider the following trial wavefunction
\[ \Psi(x) = \begin{cases} 
N(A^2 - x^2), & -A \leq x \leq A \\
0, & x < -A \text{ or } x > A 
\end{cases} \]
for the Harmonic oscillator Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$. $N$ in the above is the normalization constant, while $A$ is the variational parameter, to be determined. First
sketch the wave function for the value $A=1$. Calculate the energy $E$ as a function of $A$ for a normalized wave function, and optimize the parameter $A$, by using the variational principle. Sketch the energy as a function of $A$, clearly indicating the minimum you found and also draw in this plot the true ground state energy for the harmonic oscillator $E_0 = \frac{1}{2} \hbar \sqrt{k/m}$. Is your answer consistent with the variational principle? Why?

13. Consider an electron in one dimension that moves in the potential $V(x) = -\delta(x)$. The function $\delta(x)$ is a special function, the so-called Dirac Delta function, and we will only use the property that $\int_{-\infty}^{\infty} f(x) \delta(x) \, dx = f(0)$ for any function $f(x)$. In other words the value of the integral is the value of the function $f$ in the point $x = 0$. In this question we will use atomic units. Take as a trial wavefunction the gaussian $\Phi(x) = Ne^{-\alpha x^2}$, $\alpha \geq 0$. We further give you the following integrals $\int_{-\infty}^{\infty} e^{-\beta x^2} \, dx = \sqrt{\frac{\pi}{\beta}}$, $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} \, dx = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta}}$.

Questions:

a. Calculate the expectation value (in a.u.) for the kinetic energy and for the potential energy for a normalized function $\Phi(x)$.
b. What is the lowest value for the energy you can get for this trial wavefunction?
c. Plot the total energy as a function of $\alpha$ and verify that the value found under b is indeed a minimum.

14. a. Consider the system consisting of 1 electron and a nucleus of charge $Z$ fixed in the origin. Use atomic units and set up the one-electron Schrödinger equation for this problem. As the ground state solution try the function $e^{-\lambda r}$ and determine the ground state energy and ground state wave function. Demonstrate that your wave function satisfies your Schrödinger equation.

b. (angular momentum theory): Show that the function $\sin \theta e^{i \phi}$ is an eigenfunction of the operator $\hat{L}_z$ and of $\hat{L}^2$. What are the corresponding eigenvalues? Derive the other functions in the multiplet that have the same eigenvalue for $\hat{L}^2$. Indicate the corresponding eigenvalues for $\hat{L}_z$. 
Rovibrational problems for diatomics.

15 (a) The energy levels of a rigid rotator are \( E_J = \frac{\hbar^2}{2I}(J+1) \). Show and label the first four levels, indicate their degeneracy, and sketch the microwave spectrum of a polar diatomic that involves these lines. The observed spacing between the microwave lines of \( \text{H}^{35}\text{Cl} \) is \( 6.350 \times 10^{11} \text{ Hz} \) (21.18 cm\(^{-1}\)). Find the bond length and predict the microwave spectrum of \( \text{D}^{35}\text{Cl} \).

(b) The far infrared spectrum of \( \text{K}^{35}\text{Cl} \) has an intense line at 278.0 cm\(^{-1}\). In the harmonic oscillator approximation, find the force constant and the period of vibration of \( \text{K}^{35}\text{Cl} \).

16. A rigid rotator for rotations and a harmonic oscillator for vibrations are the simplest model of a diatomic molecule. The energy levels are (no derivation needed)

\[
E_{vJ} = \hbar \omega (v + \frac{1}{2}) + \frac{\hbar^2 J(J + 1)}{2\mu R_e^2} \quad v = 0, 1, 2..., \quad J = 0, 1, 2...
\]

a). Sketch the potential energy of the harmonic oscillator and show explicitly the lowest two vibrational levels having three rotational levels each. (Please give yourself room and be careful.) Clearly indicate which levels are close in energy and which are further apart. Indicate with arrows which transitions you would observe in a high-resolution vibrational spectrum for which \( \Delta v = 1, \Delta J = \pm 1 \). Sketch a spectrum showing three transitions of each type, and relate the spacing between lines to \( E_{vJ} \).

b). What would spectrum look like at 0.1 K, in a cold beam?

c) Suppose that \( R_e \) is different for \( v = 0 \) and \( v = 1 \); call it \( R_0 \) and \( R_1 \), with \( R_1 \) slightly larger than \( R_0 \). Discuss how the spectrum changes.
17. Consider the reaction

\[ HCl + DBr \rightarrow DCl + HBr \]

where D indicates deuterium, \(^2\text{H}\). The difference in energy between the reactant (R) and product site (P) is (almost) completely due to the difference in zero point vibrational energy. The force constant for \(^{35}\text{Cl}\) is 478 Nm\(^{-1}\), while the force constant for \(^{79}\text{Br}\) is 408 Nm\(^{-1}\). To answer the questions below take \(\mu(\text{HA}) = m_p\), \(\mu(\text{DA}) = 2m_p\) for A either Cl or Br. This problem pertains to the issue of deuterium fractionation which is sometimes discussed in biological studies. Questions:

(a) Calculate the vibrational frequencies for each of the above molecules and calculate the zeropoint energy for reactants and products using the above simplification for the reduced masses.

(b) Assume we start with 1 mole of HCl and 1 mole of DBr and wait until we achieve thermal equilibrium at \(T=300\ \text{K}\). Calculate the fraction HCl (in \%) in the sample at thermal equilibrium at \(T=300\ \text{K}\). Does Hydrogen prefer to sit in the weaker or stronger bond compared to Deuterium? Explain your answer. What would the distribution be at 0 K?

**Formal Quantum Mechanics.**

18. Consider the Hermitian operator \(\hat{A}\) (for a definition of Hermiticity see your summary) with eigenfunctions \(\psi_n(x)\) and corresponding eigenvalues \(a_n\). Questions:

(a) Show that the eigenvalues of \(\hat{A}\) are real and that the eigenfunctions corresponding to different eigenvalues are orthogonal.

(b) Under what condition (if and only if) is a linear combination \(c_n\psi_n(x) + c_m\psi_m(x)\) \((c_n\) and \(c_m\) non-zero) an eigenfunction of \(\hat{A}\)? Demonstrate your answer.

(c) Given is a normalized function \(\Phi(x) = \sum_n c_n\psi_n(x)\). Show that the average value \(\sum_j p_j a_j\) upon measurement of \(\hat{A}\) on the sample described by \(\Phi(x)\) equals the expectation value \(\int_{-\infty}^{\infty} \Phi^*(x)\hat{A}\Phi(x)dx\). Give a brief description of the measuring process and the quantum mechanical description of it incorporating the above.
Prove that the expectation value for the energy is independent of time for any arbitrary wavefunction if the Hamiltonian is independent of time. (This question has nothing to do with the previous questions regarding operator \( \hat{A} \). You can use any formal device you wish.)

19. a. Indicating your reasoning, propose trial functions for the 1s2s excited states of He and find their term symbols. Then write down the Hamiltonian operator and (without evaluating) the energy expectation value of your trial functions. Please identify contributions that are different for the singlet and triplet, and suggest why the triplet should have lower energy.

b. Find the ground-state term symbol and its degeneracy for the (3d)^3 configurations of Cr^{+3}. Indicating your reasoning, find the next lowest term and its degeneracy. In ruby lasers, we have Cr^{+3} surrounded by oxygens at \( \pm a \) along the \( x, y, \) and \( z \) axes. Indicating your reasoning, propose a d-electron wavefunction for the ground state.

20. Consider the Hamiltonian, \( \hat{H} \), with orthogonal eigenfunctions \( \phi_m(x) \) and non-degenerate eigenvalues \( E_m = m^2 B, m = 1, 2, 3, \ldots \), where \( B \) is a constant. The wavefunction is given as \( \Psi(x) = \frac{1}{\sqrt{3}} \phi_1(x) + \frac{2}{\sqrt{6}} \phi_2(x) \).

a. Show that the wavefunction is normalized. Calculate the expectation value for the energy. Also calculate \( \langle \hat{H}^2 \rangle \). What is the variance \( \sigma^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \)? Is \( \Psi(x) \) an eigenfunction of \( \hat{H} \)? Motivate your answers.

Suppose we actually do a measurement of the energy on the above wavefunction. What are the possible outcomes of this experiment? What are the probabilities to find these outcomes? What is the average value over all the outcomes? What will be the variance in the results? Should your results agree with the answers given in a? Discuss.

21. Assume the Hamiltonian \( \hat{H} = 2B \hat{S}_z \) which has the normalized eigenfunctions \( \alpha \) and \( \beta \). We will use atomic units (\( \hbar = 1 \)) and further provide the general information
\[ \hat{S}_x = \hat{S}_x + i\hat{S}_y; \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y \]
\[ \hat{S}_z \alpha = \frac{1}{2} \alpha; \quad \hat{S}_z \beta = -\frac{1}{2} \beta; \]
\[ \hat{S}_x \alpha = \hat{S}_x \beta = 0; \quad \hat{S}_- \alpha = \beta; \quad \hat{S}_+ \beta = \alpha \]

a. Using the above relations show that the normalized eigenfunctions of \( \hat{S}_x \) are
\[ \frac{1}{\sqrt{2}}(\alpha + \beta) \] and \[ \frac{1}{\sqrt{2}}(\alpha - \beta). \] What are the corresponding eigenvalues? At time \( t = 0 \) the wave function is given by \( \Psi(0) = \frac{1}{\sqrt{2}}(\alpha + \beta) \). What is the explicit expression for the wavefunction at time \( t \)? Your wave function should be oscillating in time. What is the period \( T \)?

Suppose we measure \( \hat{S}_x \) at some time \( t \) for the state described under a. What are the possible values for \( \hat{S}_x \) that can be obtained at time \( t = 0, t = T/4 \) and \( t = T/2 \), and what are the corresponding probabilities to find these outcomes. (Hint: it is most convenient to express \( \Psi(t) \) in terms of the eigenfunctions of \( \hat{S}_x \).) The spin in the x- or y-direction is said to precess under the influence of a magnetic field in the z-direction.

22. You are given a Hamiltonian \( \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \) and a time-dependent wave function
\[ \Psi(x,t) = \cos(\pi x)e^{-\frac{t^2}{2m}} + \sin(2\pi x)e^{-\frac{2\pi x^2}{m}}. \]

a. Show that \( \Psi(x,t) \) satisfies the time-dependent Schrödinger equation
\[ i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t) \]. Is the wave function at time \( t = 0 \) an eigenfunction of \( \hat{H} \)? Why or why not?

b. Sketch the wavefunction over the interval \(-\frac{1}{2} \leq x \leq \frac{1}{2}\) at times \( t = 0 \) and at time \( t = \frac{2m}{\pi \hbar} \). Also sketch the probability \( |\Psi(x,t)|^2 \) for these times. Is \( \Psi(x,t) \) a stationary state? Why or why not?
23. Consider a particle that is moving on the surface of a cylinder described by the coordinates \((x, y, z) = (R \cos \varphi, R \sin \varphi, z)\) where \(R\) is the radius of the cylinder. The \(z\) coordinate is constrained to lie between 0 and \(a\), where \(a\) is the length of the cylinder.

On the surface of the cylinder the potential is zero, and the Hamiltonian is given by

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2mR^2} \frac{\partial^2}{\partial \varphi^2}.
\]

Questions:

a.) Try as a solution for the time-independent Schrödinger equation the product function \(\Psi(\varphi, z) = f(\varphi)g(z)\), and derive differential equations for the functions \(f\) and \(g\).

b.) What are the boundary conditions associated with the differential equations under a)?

Show that the functions \(\sin\left(\frac{n\pi z}{a}\right)e^{ik\varphi}\) satisfy the time-independent Schrödinger equation.

For what values of \(n\) and \(k\) are the boundary conditions satisfied? What are the energy levels for the allowed values of \(n\) and \(k\)?

c.) Consider the special case that \(2\pi R = 2a\), i.e. the circumference of the circle is precisely the length to travel back and forth on the \(z\)-axis of the cylinder. Draw a energy level diagram of the energy levels up to and including \(10\hbar^2 / (2mR^2)\). For each energy level indicate the possible associated values of \(n\) and \(k\), and indicate the degeneracy of the energy level.