Constants:

\( h \) (Planck’s constant) = 6.6262 \times 10^{-34} \text{ J}\cdot\text{s} = 4.1352 \times 10^{-15} \text{ eV}\cdot\text{s} \\
\hbar = h/(2\pi) \\
\( c \) (speed of light) = 2.9979 \times 10^8 \text{ m/s}^{-1} \\
\( N_A \) (Avogadro’s number) = 6.022 \times 10^{-23} \text{ mol}^{-1} \\
\( \beta \) (Bohr magneton) = 9.274 \times 10^{-24} \text{ J}\cdot\text{T}^{-1} \\

Units:

1 eV = 1.6022 \times 10^{-19} \text{ J} \\
1 \text{ amu} = 1.66056 \times 10^{-27} \text{ kg} \\
1 \text{ Å} = 10^{-10} \text{ m} \\
1 \text{ N} = 1 \text{ J} \cdot \text{m}^{-1} = 1 \text{ kg} \cdot \text{m} \cdot \text{s}^{-2} \\

Hydrogen-like atom with atomic number \( Z \):

\( E_n = -\frac{Z^2e^2}{8\pi\epsilon_0a_0n^2} \) (no magnetic field) \\
\( \psi_{nlm} = Y^m_l(\theta,\phi)R_{nl}(r) \) \\
\( Y_0^0 = \frac{1}{\sqrt{4\pi}} \), \( R_{10} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \), and \( \psi_{1s} = \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \)

Possibly useful Integrals:

\[
\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}} \\
\int_0^b r^2 e^{-\alpha r} dr = \frac{2}{\alpha^3} - \frac{2}{\alpha^3} \left( 1 + b\alpha + \frac{b^2\alpha^2}{2} \right) e^{-\alpha b} \tag{1} \\
\int_b^\infty r^2 e^{-\alpha r} dr = \frac{2}{\alpha^3} \left( 1 + b\alpha + \frac{b^2\alpha^2}{2} \right) e^{-\alpha b} \tag{2}
\]
1. (10 pts) **Hydrogen.**

What is the probability of finding a 1s electron of hydrogen ($Z = 1$) within $2a_0$ of the nucleus, where $a_0$ is the Bohr radius?

**ANSWER:**

$$\int_0^{2a_0} r^2|R_{nl}(r)|^2 \, dr = \int_0^{2a_0} 4\left(\frac{Z}{a_0}\right)^3 r e^{-2Zr/a_0} \, dr$$

Let $\alpha = \frac{2}{a_0}$ and since $Z = 1$,

$$... = \frac{4}{a_0^3} \int_0^{2a_0} r^2 e^{-\alpha r} \, dr = \frac{4}{a_0^3} \left[ \frac{2}{\alpha^3} - \frac{2}{\alpha^3} \left( 1 + 2a_0\alpha + \frac{4a_0^2\alpha^2}{2} \right) e^{-2a_0\alpha} \right]$$

$$= \frac{4}{a_0^3} \left[ 1 - 13e^{-4} \right] = 1 - 13e^{-4} = 0.762$$

2. (10 pts) **Virial Theorem.**

a) Write the equation for the quantum mechanical virial theorem and use it to determine the kinetic energy of the hydrogen-like atom in terms of the potential energy.

**ANSWER:**

$$<x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} >= 2 < \hat{K} >$$

or $n < \hat{V} >= 2 < \hat{K} >$ or $\hat{V} = Cr^n$

b) Use the virial theorem to determine the value of the kinetic energy for the ground state of the hydrogen-like atom. You can use the expression for the total energy of the hydrogen-like atom given on the front page.

**ANSWER:**

From a) we have $< \hat{K} >= -\frac{1}{2} < \hat{V} >$,

Since $<E> = <\hat{K}> + <\hat{V}>$, $<\hat{K}> = -\frac{1}{2} \left( <E> - <\hat{K}> \right)$

So, $<\hat{K}> = - <E> = \frac{Z^2e^2}{8\pi\epsilon_0a_0}$ for $n = 1$
3. **(10 pts) Variational principle.**

Consider the trial wave function \( \phi = e^{-\alpha r} \), where \( \alpha \) is a parameter. State the quantum mechanical variational principle (either by a formula or in words), and use it (i.e. solve for \( \alpha \)) to estimate the ground state energy and wave function for the hydrogen-like atom (show your work).

\[
\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{3}
\]

Some useful integrals are:

\[
\int e^{-\alpha r} \hat{H} e^{-\alpha r} d^3r = \frac{e^2 a_0}{8\epsilon_0\alpha} - \frac{Ze^2}{4\epsilon_0\alpha^2} \tag{4}
\]

where \( a_0 \) is the Bohr radius, and

\[
\int e^{-2\alpha r} d^3r = \frac{\pi}{\alpha^3} \tag{5}
\]

\[
E[\phi] = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \left[ \frac{e^2 a_0}{8\epsilon_0\alpha} - \frac{Ze^2}{4\epsilon_0\alpha^2} \right] \frac{\alpha^3}{\pi} = \frac{e^2 a_0\alpha^2}{8\epsilon_0\pi} - \frac{Ze^2\alpha}{4\pi\epsilon_0}
\]

\[
\frac{dE}{d\alpha} = \frac{e^2 a_0\alpha}{4\pi\epsilon_0} - \frac{Ze^2}{4\pi\epsilon_0} = 0
\]

\[
\alpha = \frac{Z}{a_0}
\]

\[
E_{\text{min}} = -\frac{Z^2e^2}{8\epsilon_0 a_0\pi}
\]
4. (10 pts) **Perturbation theory.**

a) Given the Hamiltonian for a 1-dimensional *quartic* oscillator:

\[ \hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + cx^4 \]  

(6)

What is the formula for the first order energy correction \( E_n^{(1)} \) based on the wave function \( \psi_n^{(0)} \) for the *harmonic* oscillator Hamiltonian with potential energy \( (1/2)kx^2 \)? (Make sure you correctly identify \( \hat{H}^{(1)} \) - you don’t have to calculate any integrals, just write the formula).

**ANSWER:**

\[ E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}^{(1)} \psi_n^{(0)} \, d\tau, \text{ with } \hat{H}^{(1)} = cx^4 - \frac{1}{2}kx^2. \]

b) What is the formula for the first order correction to the wave function \( \psi_n^{(1)} \) (identify all terms)?

**ANSWER:**

\[ \psi_n^{(1)} = \sum_{k \neq n} \frac{\hat{H}^{(1)}_{kn}}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)}, \text{ with } \hat{H}^{(1)}_{kn} = \int \psi_k^{(0)*} H^{(1)} \psi_n^{(0)} \, d\tau. \]

5. (10 pts) **Many-electron systems.**

a) Write the Hamiltonian for an N-electron atom with nuclear charge \( Z \). Identify the kinetic energy, nuclear attraction, and electron-electron repulsion terms. Use either atomic units or SI units.

\[ \hat{H} = \sum_{i=1}^{N} -\frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]

\( \underline{\text{kin. ener.}} \quad \underline{\text{nuc. attr.}} \quad \underline{\text{elec. repul.}} \)
b) Which of the following are valid wave functions in terms of the spin-orbitals $\psi(x)$ according to the Pauli principle?

a. $\Psi = \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N) \end{vmatrix}$

b. $\Psi = \psi_1(x_1)\psi_2(x_2)$

c. $\Psi = \psi_1(x_1)\psi_1(x_2) - \psi_2(x_1)\psi_2(x_2)$

d. $\Psi = \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)$

only A and D are valid

6. (10 pts) **Term symbols.**

Give the ground state term symbols for

a) phosphorus \([\text{Ne}]3s^23p^3\)

\[
\begin{array}{cccc}
\uparrow & \uparrow & \uparrow \\
-1 & 0 & 1
\end{array}
\]

\[
m_s = \frac{3}{2} \rightarrow \left[ S = \frac{3}{2} \right]
\]

\[
m_\ell = 0 \rightarrow \left[ L = 0 \rightarrow S \right]
\]

\[
J = 0 + \frac{3}{2}, \ldots, \left| 0 - \frac{3}{2} \right| = \frac{3}{2}
\]

\[{}^4S^{3/2}_2\]

b) vanadium \([\text{Ar}]4s^23d^3\)

\[
m_s = \frac{3}{2} \rightarrow \left[ S = \frac{3}{2} \right]
\]

\[
m_\ell = 3 \rightarrow \left[ L = 3 \rightarrow F \right]
\]

\[
J = 3 + \frac{3}{2}, \ldots, \left| 3 - \frac{3}{2} \right| = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}
\]

Shell is $< \frac{1}{2}$ filled $\therefore$ smallest $J$ is the ground state.

\[{}^4F^3_2\]
7. (10 pts) **Atomic spectra.**

Some of the electronic states of sodium are designated by the term symbols:

\[ \text{1}S_{1/2}, \text{2}P_{3/2}, \text{2}P_{1/2}, \text{2}D_{3/2}, \text{2}F_{5/2} \]

What are the allowed transitions between these states according to the selection rules for atomic spectra?

**SELECTION RULES:**

\[ \Delta L = \pm 1 \]

\[ \Delta J = 0, \pm 1, \text{ but } J = 0 \not\rightarrow J = 0 \]

\[ \Delta S = 0 \]

**ALLOWED TRANSITIONS:**

\[ \text{2}P_{3/2} \rightarrow \text{2}D_{5/2} \text{ because } \Delta S = 0, \Delta L = 1, \Delta J = 0 \]

\[ \text{2}P_{1/2} \rightarrow \text{2}D_{3/2} \text{ because } \Delta S = 0, \Delta L = 1, \Delta J = 1 \]

\[ \text{2}D_{3/2} \rightarrow \text{2}F_{5/2} \text{ because } \Delta S = 0, \Delta L = 1, \Delta J = 1 \]

8. (10 pts) **Electronic states.**

a) How many total electronic states are possible for a \(4f^{12}\) electronic configuration?

\[
\frac{G!}{N!(G-N)!} = \frac{14 \cdot 13 \cdot 12 \cdot \ldots \cdot 1}{12 \cdot 11 \cdot \ldots \cdot 1 \cdot (2 \cdot 1)} \\
= \frac{14 \cdot 13}{2} = 91 \text{ states}
\]

b) How many electronic states are associated with a \(3D\) term symbol (how many sets of magnetic quantum numbers \(m_l\) and spin quantum numbers \(m_s\))? 

\[
(2l + 1)(2s + 1) = (2 \cdot 2 + 1)(2 \cdot 1 + 1) \\
= 5 \cdot 3 = 15 \text{ states}
\]
(4 pts) **Extra credit.**

True/False

Every linear combination of solutions of the time-independent Schrödinger equation is also a solution of this equation.

**FALSE**

Every linear combination of solutions of the time-dependent Schrödinger equation is also a solution of this equation.

**TRUE**