This exam is structured just like our three hour exam which will be closed book and with closed notes. You may refer to your single-sided 8½” × 11” crib sheet. In the actual final exam you will be asked to draw a box around your final answers, where applicable.

**Constants**

- **mass of the electron** \( m = 9.10939 \times 10^{-28} \text{ g} = 9.10939 \times 10^{-31} \text{ kg} \)
- **charge of the proton** \( e = 4.8032 \times 10^{-10} \text{ g}^{1/2} \text{ cm}^{3/2} \text{ s}^{-1} = 1.602177 \times 10^{-19} \text{ C} \)
- **Planck’s constant / \( \pi \)** \( h = 1.05457 \times 10^{-27} \text{ g cm}^{2} \text{ s}^{-1} = 1.05457 \times 10^{-34} \text{ J s} \)
- **Bohr radius** \( a_0 = 5.291772 \times 10^{-9} \text{ cm} = 5.291772 \times 10^{-11} \text{ m} \)

**Formulae**

The energies and wavefunctions for a particle of mass \( m \), in a one-dimensional box of length \( a \), and with infinitely high walls are \( E_n = \frac{n^2 \hbar^2}{8ma^2} \), and \( \psi_n(x) = \frac{2}{a} \sqrt{\frac{1}{a}} \sin\left(\frac{n\pi x}{a}\right) \), where \( n \) is an integer.

1s wavefunction of hydrogen: \( \psi_{1s}(r, \theta, \phi) = \left(\frac{1}{\pi^{1/2}}\right)\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} \)

radial probability function: \( P(r)dr = 4\pi r^2\psi^2(r)dr \)

First order correction to the energy:

If \( H = H^0 + H^{(1)} \), and \( E_n = E_n^0 + E_n^{(1)} \), then \( E_n^{(1)} = <\psi_n^0|H^{(1)}|\psi_n^0> \)

Diagonalizing a 2×2 matrix:

\[
H_{\text{diag}} = U^T H U = \begin{pmatrix}
\cos(\theta) & \sin(\theta) \\
-\sin(\theta) & \cos(\theta)
\end{pmatrix}
\begin{pmatrix}
a & b \\
b & c
\end{pmatrix}
\begin{pmatrix}
\cos(\theta) & -\sin(\theta) \\
\sin(\theta) & \cos(\theta)
\end{pmatrix}
\]

where \( \tan(2\theta) = \frac{2b}{a-c} \), and the columns of \( U \), the unitary matrix on the right, are the new wavefunctions (vectors) in terms of the original vectors. The first column of \( U \) corresponds to the upper left eigenvalue of \( H_{\text{diag}} \).

\[
J^2 |J, L, S> = J(J + 1)\hbar^2 |J, L, S>
\]
\[
L^2 |J, L, S> = L(L + 1)\hbar^2 |J, L, S>
\]
\[
S^2 |J, L, S> = S(S + 1)\hbar^2 |J, L, S>
\]

\[
J_+ |j, m> = [(j + 1) - m(m + 1)]^{1/2} \hbar |j, m + 1>
\]
\[
J_- |j, m> = [(j + 1) - m(m - 1)]^{1/2} \hbar |j, m - 1>
\]

These are general formulae for the raising and lowering operators for angular momentum.
1. A one dimensional box with potential walls of $V = \infty$ at $x = 0$ and at $x = a$ is perturbed as shown in the figure:

The potential is 0 from $x = 0$ to $x = a/2$, and is a small constant, $\hbar^2/(80m a^2)$, from $x = a/2$ to $x = a$. The potential is $\infty$ for $x \leq 0$ and is $\infty$ for $x \geq a$. The __________ is the perturbation.

Use first order perturbation theory to calculate the correction that must be added to the zeroth order eigenvalues of the particle in a box with infinite walls and no perturbation inside. Do this in general for all $n$, where $n$ is the quantum number for the particle in a box. Write down the total energy (zeroth order plus first order correction) in general for all $n$. [Hint you may refer to the attached integral table].

2. In class and in your homework we showed that for the two electron atom (He), the $S = 0$, $M_S = 0$ coupled state is

$$|S, M_S> = |0, 0> = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(2)\alpha(1)]$$ (1)

where $\alpha$ is the one-electron $s = 1/2$, $m_s = +1/2$, and $\beta$ is the one-electron $s = 1/2$, $m_s = -1/2$ wavefunction. The numbers in parentheses are the electron number, either electron number 1 or electron number 2.

For the He triplet state, we know that

$$|S, M_S> = |1, +1> = \alpha(1)\alpha(2)$$ (2)

The coupled two-electron spin lowering operator $S_z$ is simply written as the scalar sum of the two one-electron lowering operators $s_1$ and $s_2$.

$$S_z = s_1 + s_2.$$ (3)

Use equation (3) on (both sides, middle and right) of equation (2) to generate the correct, normalized, coupled, two-electron wavefunction $|S, M_S> = |1, 0>$ in terms of the one electron $\alpha$ and $\beta$ functions.
3. The energies of a diatomic molecule were calculated in class from the linear combination of atomic orbitals (LCAO) model and applying the variational principle to find the wavefunctions $|\psi> = c_1|a> + c_2|b>$ that gave the lowest energies after adjusting $c_1$ and $c_2$. The $|a>$ and $|b>$ are the atomic orbitals centered on atoms a and b. These energies are (for homonuclear diatomics)

$$E_+ = (\alpha + \beta)/(1 + S)$$  \hspace{1cm} \text{bonding orbital energy} \hspace{1cm} (1)

and

$$E_- = (\alpha - \beta)/(1 - S)$$  \hspace{1cm} \text{antibonding orbital energy} \hspace{1cm} (2)

where $\alpha = <a|H|a> = <b|H|b>$, \hspace{1cm} (3a)

$\beta = <a|H|b> = <b|H|a>$ which is less than zero, and \hspace{1cm} (3b)

the overlap, $S = <a|b> = <b|a>$ is a small, but non-zero, positive number. \hspace{1cm} (3c)

We can obtain (almost) the same results by the simple expedient as setting up the problem as a 2×2 Hamiltonian matrix by assuming $S = 0$ (and therefore, $|a>$ and $|b>$ are orthonormal).

(a) Set up and diagonalize this 2×2 Hamiltonian matrix and obtain the energies of the lowest bonding and antibonding orbitals of a homonuclear diatomic orbital. Assume $S = 0$. Remember, $\beta < 0$.

(b) Using the unitary (orthogonal, really, since they are real) matrix used in your diagonalization of part (a), write down the normalized bonding wavefunction $|\psi_+>$ that corresponds to the energy $E_+$ that you calculated in (a) in terms of the basis functions $|a>$ and $|b>$. Also, write down the normalized antibonding wavefunction $|\psi_->$ that corresponds to the energy $E_-$ that you calculated in (a) in terms of the basis functions $|a>$ and $|b>$.

4. Diatomic Rotational Spectroscopy

$E = B J(J + 1)$

$B = \hbar^2/(2 I)$  \hspace{1cm} \text{in units of energy}

$I = \mu r^2$

$\mu = m_1 m_2/(m_1 + m_2)$

atomic mass unit (amu) = $1.66054 \times 10^{-24}$ g = $1.66054 \times 10^{-27}$ kg

$m(^1\text{H}) = 1.007825$ amu

$m(^35\text{Cl}) = 34.968851$ amu

The spacing between the transitions in the microwave spectrum of $^3\text{H}^35\text{Cl}$ is approximately $6.350 \times 10^{11}$ Hz (635.0 GHz). Calculate the bond length of HCl. [While this is fundamentally a straight-forward problem, you have to be careful with the units].