Key

Your name: ________________________________

Student ID#: ________________________________

I have neither received nor provided assistance of any kind on this exam.

Signature: ________________________________

I attend lecture/discussion on average: <1, 1-2, 2-3, 3-4 times per week
(your answer to this questions will not affect your grade)

I want this exam to be left in the hallway for collection: YES / NO

In the following, u and v are functions of x, and a and n and m are real numbers

\[ \int u\,dv = uv - \int v\,du \]

\[ \int x^n\,dx = \frac{x^{n+1}}{n+1} \quad \text{except}\ n = -1 \]

\[ \frac{d}{dx}\ln x = \frac{1}{x} \]

\[ \int e^x\,dx = e^x \]

\[ \int \sin ax\,dx = -\frac{1}{a}\cos ax \]

\[ \int \cos ax\,dx = \frac{1}{a}\sin ax \]

\[ \int \sin ax\,dx = -\frac{1}{a}\cos ax \]

\[ \int \cos ax\,dx = \frac{1}{a}\sin ax \]

\[ \int (\sin ax)^m\,dx = \frac{1}{a}\left[ \frac{(\sin ax)^{m+1}}{m+1} \right] = 0 \quad \text{for}\ m = 0 \]

\[ \int (\cos ax)^m\,dx = \frac{1}{a}\left[ \frac{(\cos ax)^{m+1}}{m+1} \right] = 0 \quad \text{for}\ m = 0 \]

\[ \int e^{ax}\,dx = \frac{1}{a}e^{ax} \quad (a > 0, n\text{ positive integer}) \]

\[ \int e^{-ax}\,dx = \frac{1}{-a}e^{-ax} \]

\[ \int x^{n-1}\,dx = \frac{x^n}{n} \quad (n \neq 0) \]

\[ \int x^{m-1}\,dx = \frac{x^m}{m} \quad (m \neq 0) \]

\[ \int e^{ax}\cdot f(x)\,dx = \frac{e^{ax}}{a}\left[ f(ax) \right] \]
The First Few Spherical Harmonics

\[
Y_0^0 = \frac{1}{\sqrt{4\pi}} \\
Y_1^0 = \frac{3}{2\sqrt{2\pi}} \cos \theta \\
Y_1^1 = \frac{3}{2\sqrt{2\pi}} \sin \theta e^{i\phi} \\
Y_{-1}^1 = -i \frac{3}{2\sqrt{2\pi}} \sin \theta e^{-i\phi} \\
Y_2^0 = \frac{5}{16\sqrt{6\pi}} (3 \cos^2 \theta - 1) \\
Y_1^2 = \frac{15}{8\sqrt{2\pi}} \sin \theta \cos \theta e^{i\phi} \\
Y_{-1}^2 = -i \frac{15}{8\sqrt{2\pi}} \sin \theta \cos \theta e^{-i\phi} \\
Y_2^1 = \frac{15 i}{8\sqrt{2\pi}} \sin^2 \theta e^{2i\phi} \\
Y_{-2}^1 = - \frac{15 i}{8\sqrt{2\pi}} \sin^2 \theta e^{-2i\phi}
\]

Question 1: _______/10
Question 2: _______/20
Question 3: _______/30
Question 4: _______/10
Question 5: _______/30

Total: _______/______

Potentially Useful Information:

Workfunctions of Metals:
- Li 2.3 eV
- Ca 2.87 eV
- Al 4.28 eV
- Au 5.1 eV

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Atomic mass constant</td>
<td>m_u</td>
<td>1.660 5402 x 10^{-27} kg</td>
</tr>
<tr>
<td>Avogadro constant</td>
<td>N_A</td>
<td>6.022 1376 x 10^{23} mol^{-1}</td>
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<tr>
<td>Bohr magneton</td>
<td>μ_B</td>
<td>9.274 0154 x 10^{-28} J \cdot T^{-1}</td>
</tr>
<tr>
<td>Bohr radius</td>
<td>a_B</td>
<td>2.817 3561 x 10^{-10} m</td>
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<tr>
<td>Boltzmann constant</td>
<td>k_B</td>
<td>1.380 658 x 10^{-23} J \cdot K^{-1}</td>
</tr>
<tr>
<td>Electron rest mass</td>
<td>m_e</td>
<td>9.109 3897 x 10^{-31} kg</td>
</tr>
<tr>
<td>Gravitational constant</td>
<td>G</td>
<td>6.672 59 x 10^{-11} m^3 \cdot kg^{-1} \cdot s^{-2}</td>
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<tr>
<td>Molar gas constant</td>
<td>R</td>
<td>8.3145101 J \cdot K^{-1} \cdot mol^{-1}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.083 1451 dm^3 \cdot bar K^{-1} \cdot mol^{-1}</td>
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<tr>
<td></td>
<td></td>
<td>0.082 0578 dm^3 \cdot atm K^{-1} \cdot mol^{-1}</td>
</tr>
<tr>
<td>Molar volume, ideal gas</td>
<td>(one bar, 0°C)</td>
<td>22.711 06L \cdot mol^{-1}</td>
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<tr>
<td></td>
<td>(one atm, 0°C)</td>
<td>22.441 09L \cdot mol^{-1}</td>
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<tr>
<td>Nuclear magneton</td>
<td>μ_n</td>
<td>5.050 7666 x 10^{-27} J \cdot T^{-1}</td>
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<td>Permittivity of vacuum</td>
<td>ε_0</td>
<td>8.854 187 816 x 10^{-12} C^2 \cdot J^{-1} \cdot m^{-1}</td>
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<td>Planck constant</td>
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<td>6.626 0755 x 10^{-34} J \cdot s</td>
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<tr>
<td>Proton charge</td>
<td>e</td>
<td>1.602 177 33 x 10^{-19} C</td>
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<td>Proton magnetogyc ratio</td>
<td>g_p</td>
<td>2.675 221 26 x 10^6 s^{-1} \cdot T^{-1}</td>
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<tr>
<td>Proton rest mass</td>
<td>m_p</td>
<td>1.672 6231 x 10^{-27} kg</td>
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<tr>
<td>Rydberg constant (Bohr)</td>
<td>R_n</td>
<td>2.179 8736 x 10^{-13}</td>
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<tr>
<td>Rydberg constant for H</td>
<td>R_H</td>
<td>109 737.31534 cm^{-1}</td>
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<tr>
<td>Speed of light in vacuum</td>
<td>ε</td>
<td>299 792 458 m \cdot s^{-1} (defined)</td>
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<tr>
<td>Stefan-Boltzmann constant</td>
<td>σ</td>
<td>5.670 51 x 10^8 J \cdot m^{-2} \cdot K^{-1} \cdot s^{-1}</td>
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</table>
1). Rigid rotor and spherical Harmonics (10 points)
We can visualize the shape of the spherical harmonics by plotting them in 3D using the format: \( r = Y_l^m(\theta, \phi) \).

1a) We know that the spherical harmonics are the solutions to the Schrödinger equation for the diatomic rigid rotor. Order the rigid rotor wave functions shown below from lowest to highest energy. ( eg. A, B, C) (3 points)

\[ \begin{align*}
B &< C < A \\
&\text{right or wrong order}\text{ } +3 \text{ or } 0
\end{align*} \]

1b) Explain your choice of ordering based on the shapes in the figures below, in particular what that tells you about the kinetic energy. (7 points)

2) Hydrogen atom wave functions and their interpretation in 3-dimensions (20 points)

The wavefunction for the ground state of the H atom is: \( \psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-r/a_0} \)

2a) Sketch the radial probability distribution (probability of finding the electron at some distance between \( r \) and \( r+dr \) from the nucleus) for an electron in the \( \psi_{100} \) state. Be sure to CALCULATE (and label your sketch with) the most probable value of \( r \) for this state. (15 points)

\[ \begin{align*}
\int_{0}^{\infty} P(r)dr &\approx \frac{4r^2}{a_0^3} e^{-2r/a_0} \\
\text{max} \text{ when } \frac{dP}{dr} &= 0 = \frac{8r}{a_0^3} e^{-2r/a_0} - \frac{8r^3}{a_0^3} e^{-2r/a_0} \\
&= \frac{8r e^{-2r/a_0}}{a_0} \left( 1 - \frac{r}{a_0} \right)
\end{align*} \]

\[ \frac{r_{\text{max}}}{a_0} = 1 \]

10 for \( a_0 \) value
2b) For the H-atom, the electron energy depends ONLY on the principle quantum number n (i.e. the energy of the 2s state is the same as the 2p state). For heavier atoms, this is not the case. Explain why the energy of an electron depends on angular momentum (why the energies are ordered \( s < p < d < f \)) for atoms heavier than H but not for H. (5 points)

The effect is due to more electron repulsion and screening concept.

1c) high \( l \) orbitals distribute e- probability farther from nucleus where they penetrate the inner orbitals less and experience a reduced nuclear charge \( \Rightarrow \) lower energy.

3) Multi-electron Atoms (30 points)
3a) Work out (simply listing is unacceptable) the possible term symbols for the \( 1s^2 2s^2 2p^6 \) configuration of O (including the possible J values). (13 points)

<table>
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<tr>
<th>( m_s )</th>
<th>( m_l )</th>
<th>( M_s )</th>
<th>( M_l )</th>
<th>( M_{\text{tot}} )</th>
<th>( M_{\text{total}} )</th>
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</tr>
</tbody>
</table>

\[ \sum_{j=0}^{5} \begin{pmatrix} 6! \end{pmatrix} = 15 \text{ states} \]

\[ L=2 \quad S=0 \Rightarrow \text{D term } J=2 \]

\[ L=1 \quad S=1 \Rightarrow \text{3p term } J=2, 1, 0 \]

\[ L=0 \quad S=0 \Rightarrow \text{S term } S=0 \]

Terms: 5 points for nun 6 for levels

\[ 1\text{D}_{2}, 3\text{p}_{3}, 3\text{p}_{1}, 3\text{p}_{0}, 1\text{S}_{0} \]

5 points only if no work

3b) Rank the terms and levels from left to right in order from LOWEST to HIGHEST energy (level is the term symbol with total J included). EXPLAIN (briefly). (5 points)

A half-filled orbital \( \Rightarrow \) largest \( S \) lowest in energy, \( \text{within a term} \)

\[ 3\text{p}_{3} < 3\text{p}_{1} < 3\text{p}_{0} < 1\text{D}_{2} < 1\text{S}_{0} \]

3c) Passing through a rift in the fabric of space time (yet again), the crew of the Enterprise find themselves in a universe where + and - charge attract according to Coulomb’s law, but - charges no longer repel one another. The electrons in this universe possess spin angular momentum (and obey the Pauli principle), but possess no magnetic moment. In this strange universe, re-rank the relative energy differences between the terms and levels you’ve written above (use = to indicate any that are equal).

(Data remarks: “Captain, its as if the interelectron repulsion and spin-orbit coupling terms in the atomic Hamiltonian have been made zero!”) (6 points)

\[ 3\text{p}_{3} = 3\text{p}_{1} = 3\text{p}_{0} = 1\text{D}_{2} = 1\text{S}_{0} \]
d) What are the possible terms and levels for the 1s^22s^22p^64s^23d^{10}4p^{4} configuration of Se? (you may simply state the answer if you know them based on your work above) (3 points)

\[ Ld_{2}, \quad 3P_{2}, \quad 3P_{1}, \quad 3P_{0}, \quad 1S_{0} \quad (same \ as \ 0) \]

e) Considering the magnitude of the spin-orbit coupling term, would the energy difference between the lowest two levels be larger or smaller for Se than for O? Why (very short answer)? (3 points)

\[ \hat{H}_{so} \neq \hat{Z}^4 \Rightarrow \text{level splitting is larger for Se} \]

4) In 1971 a paper was published that applied the variational function \( N e^{-\frac{(b_1^2/a_0^2 - c_1)}{a_0}} \) to the hydrogen atom (where \( N \) is a normalization constant, \( b \) and \( c \) are variational parameters). The paper claimed that minimization of the variational energy with respect to the parameters \( b \) and \( c \) yielded an energy 0.7% above the true ground state energy of H). Why must the paper be incorrect? (10 points)

\[ Ne^{-\frac{cr/a_0}{a_0}} \] is the form of the H-atom

(\text{true}) \quad \because \text{since the } \Phi_{\text{trial}} \text{ contains this term a variational approach should return } E_{\text{true}} \text{, i.e. 0% error}

5) Rotational/Vibrational Spectra (30 points)

5a) What is/are the selection rule(s) for the transitions between rotational states of a linear diatomic molecule? (2 points)

\[ \Delta \ell = \pm 1 \]

5b) Give one physical motivation/interpretation to the selection rule in (a) (2 points)

conservation of angular momentum of the photon

with \( \ell = 1 \)

An experimental high-resolution IR spectrum for HCl is included on the last page of the exam. The units are displayed in wavenumbers. (you may tear it off for study if you wish).

5c) In two-three sentences, explain why we see a series of lines rather than a single vibrational peak in the high-resolution spectrum? (5 points)

rotational transitions accompany vibrational transitions, the \( \Delta\ell = \pm 1 \) selection rule leads to a series of evenly spaced rotational transitions superimposed on the vibrational spectrum (\( \Delta n = 1 \)) (and the absence of the \( \Delta n = 2 \) \( \Delta \ell = 0 \) peak) because many \( \ell \) states are populated a room T
5d) Calculate the bond length of an HCl molecule using the data in the graph. (10 points)

\[ \text{read from graph, spacing = } 2B \approx 19.66 \text{ cm}^{-1} \text{ for } ^1H^35\text{Cl peaks} \]
\[ (= 3.899 \times 10^{-22} \text{ J}) \]
\[ \text{in cm}^{-1} \quad B = \frac{h}{8\pi^2 \varepsilon_0 C l} \]
\[ \gamma = \sqrt{\frac{h}{8\pi^2 C \mu \beta}} = \sqrt{\frac{6.626 \times 10^{-34} \text{ J}s}{8 \pi^2 (3 \times 10^{10} \text{ kg/s})(1.61 \times 10^{-27} \text{ kg})}(9.83 \text{ cm}^{-1})} \]
\[ M = \frac{1}{3} \times 1.33 \times 1.66 \times 10^{-27} \text{ kg} \]
\[ = 1.32 \times 10^{-27} \text{ kg} \]

Length:
\[ 1.32 \times 10^{-10} \text{ m} = 1.32 \text{ Å} \]

e) How would the spectrum of pure $^1H^35\text{Br}$ gas be different from the spectrum shown for HCl? (consider specifically i) the position/energy of the central peak (higher, lower, why?), ii) the spacing between the peaks, iii) the number of peaks, and if transitions from states with the same initial and final $J$ values will be split and if so, by how much). (11 points)

i) $^3\text{Br}$ is heavier (large) and has a weaker bond (lower $v$)
both shift $\Delta J$ peaks to lower energy $\Delta E = \hbar \sqrt{\frac{K}{\mu}}$

ii) Spacing due to rotational transitions goes down
bond length increases $\oplus M$ goes up $\Rightarrow$ (larger $I$)

\[ \Delta E \approx \frac{\hbar^2}{2l(l+1)} \]

iii) The splitting within the rotational peaks is due to
the shift in vibrational energy due to the presence of
2 isotopes of Cl - pure $^1H^35\text{Br}$ will have no isotope splitting

Note: all underlined effects must be mentioned to receive full credit.