Name ________________________

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April 7th, 2025

Chemistry 120A - Second Midterm Exam

This exam consists of four questions for a total of 100 points. **An equation sheet is given in the back of this exam.** Review the point distribution before starting the exam and read the entire question prompt - it may contain hints. **Your solutions need to be on the front pages of the exam - the back of the pages can be used as scratch paper, but will not be considered for grading.**

1. 21pts - **Multiple Choice.** Fill in the circle of the **ONE** correct answer. Scratch paper is provided on the next page; **only color one circle** on this sheet. Any answers on other sheets will not be graded.

   (a) **The energetic degeneracy for hydrogen-like atoms to zeroth order and energy defined by the principle quantum number n is...**

   ○ n^2.
   ○ $2n + 1$.
   ○ depends on the nucleus.

   Explanations: Quantum numbers n, l, m can take

   $l = 0, 1, \ldots, n-1 \qquad m = -l, \ldots, l$

   (b) **The hydrogen-like orbital function $\Psi_{210}(r, \theta, \phi)$ (the $2p_z$ orbital) has...**

   ○ only angular nodes.
   ○ one angular node and one radial node.
   ○ two angular nodes and two radial nodes.

   (c) **The radial wavefunction for the electron in hydrogen-like atoms...**

   ○ depends on quantum numbers n and m_l.
   ○ depends on n only.
   ○ depends on quantum numbers n and l.

   Explanations: $R_{nl}(r)$

   (d) **If the component of the angular momentum of a particle in the x-direction of a chosen framework is known,**

   ○ the total angular momentum is equal to l_x.
   ○ the system is in an Eigenstate of $\hat{l}^2$.
   ○ $\hat{l}_y$ and $\hat{l}_z$ can be known with unconstrained precision.

   Explanations:

   A, wrong. It should be l^2.

   B, correct. $[\hat{l}_x, \hat{l}^2] = 0$.

   C, wrong. $[\hat{l}_x, \hat{l}_y] \neq 0$, $[\hat{l}_x, \hat{l}_z] \neq 0$.

(e) **A valid two-electron wavefunction for the He ground state ($1s^2$ electron configuration) must reflect the indistinguishability of electrons and have the correct symmetry under permutation of electrons. Which wavefunction is valid?**

○ $\Psi = 1s(1)1s(2)\alpha(1)\alpha(2)$
○ $\Psi = 1s(1)1s(2)[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$
○ $\Psi = 1s(1)1s(2)[(\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

Explanations: Antisymmetry for Fermionic wavefunctions

(f) **A Stern-Gerlach device prepares a beam of Ag atoms (s=1/2) in the "spin up" state by discarding atoms with "spin down" (in the z direction). What is true about a subsequent measurement of the spin in the x-direction?**

○ The expectation value is $\frac{1}{2}\hbar$.
○ The Ag atoms are deposited in one spot.
○ The Eigenvalue of the $\hat{s}^2$ operator remains unchanged.

Explanations:

A, wrong. $P_{\uparrow_x} = P_{\downarrow_x} = 0.5$. The expectation value should be 0.

B, wrong. As above, they should be at two spots.

C, correct. The expectation value of $\hat{s}^2$ is always $3/4\hbar^2$.

(g) **Several particles with spin are occupying the same spatial orbital. The particles are Fermions with a spin quantum number of $\frac{3}{2}$. What's true?**

○ There must be strong spin-orbit coupling.
○ No more than two particles can be in the same spatial orbital.
○ No more than four particles can be in the same spatial orbital.

Explanations:

$s = \frac{3}{2}, \qquad m_s = \pm\frac{3}{2}, \pm\frac{1}{2}$

2. 19pts - **Perturbation on a particle-on-a-ring.** Consider a particle of mass m confined to move freely on a circular ring of radius r, centered at the coordinate origin $(0,0)$. A small perturbation potential is added, which yields the total Hamiltonian of this system to be

$$\hat{H}(\phi) = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2} + rF(\cos\phi + \sin\phi + 1),$$

where F is a constant in units energy/length.

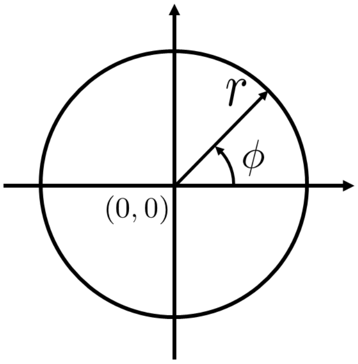

Figure 1: Coordinate for the particle on a ring.

(a) Identify and write out explicitly the unperturbed Hamiltonian $\hat{H}^{(0)}(\phi)$ and the perturbative part $\hat{H}^{(1)}(\phi)$ based on $\hat{H}(\phi)$.

The total Hamiltonian is

$$\hat{H}(\phi) = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2} + rF\Big(\cos\phi + \sin\phi + 1\Big).$$

We can identify the unperturbed Hamiltonian and the perturbation as follows:

$$\hat{H}^{(0)}(\phi) = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2},$$

$$\hat{H}^{(1)}(\phi) = rF\Big(\cos\phi + \sin\phi + 1\Big).$$

(b) Given the zeroth-order Eigenfunctions for $\hat{H}^{(0)}(\phi)$

$$\psi^{(0)}(\phi) = \frac{1}{\sqrt{2\pi}} e^{+im_l\phi},$$

show that the first-order energy correction due to $\hat{H}^{(1)}(\phi)$ is

$$E^{(1)} = Fr$$

for all quantum numbers m_l.

The first-order energy correction for a given unperturbed eigenstate $\psi^{(0)}_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$ is given by

$$E^{(1)}_{m_l} = \langle \psi^{(0)}_{m_l} | \hat{H}^{(1)} | \psi^{(0)}_{m_l} \rangle = \int_0^{2\pi} \psi^{(0)*}_{m_l}(\phi)\, \hat{H}^{(1)}(\phi)\, \psi^{(0)}_{m_l}(\phi)\, d\phi.$$

Substituting in the expressions for $\psi^{(0)}_{m_l}(\phi)$ and $\hat{H}^{(1)}(\phi)$ we have:

$$E^{(1)}_{m_l} = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im_l\phi} \Big[rF(\cos\phi + \sin\phi + 1) \Big] \frac{1}{\sqrt{2\pi}} e^{im_l\phi}\, d\phi.$$

Since

$$\frac{1}{\sqrt{2\pi}} e^{-im_l\phi} \cdot \frac{1}{\sqrt{2\pi}} e^{im_l\phi} = \frac{1}{2\pi},$$

this becomes

$$\begin{aligned} E^{(1)}_{m_l} &= rF \frac{1}{2\pi} \int_0^{2\pi} \Big(\cos\phi + \sin\phi + 1 \Big)\, d\phi \\ &= rF \frac{1}{2\pi} \Big(0 + 0 + 2\pi \Big) = rF. \end{aligned}$$

Hence, the first-order energy correction is

$$E^{(1)} = rF,$$

which is the same for all quantum numbers m_l.

3. 30pts - **H-atom and variational calculations**. We consider the effects of charging on the electronic ground state energy of atomic hydrogen.

   (a) Write down the Hamiltonian for the H atom. Assume the nucleus is stationary. Clearly define the used coordinate system and spatial variables. You may chose to indicate the distances between particles in a drawing. Include any needed physical constants and name them.

   $$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r},$$

   where m_e (or μ) is the mass (or reduced mass) of the electron, ∇_e^2 is the Laplacian of the electron, e is the electron charge, r is the separation between the electron and the nucleus. $\hbar$ and ε_0 are defined as convention.

   (b) The energy of the electron in the ground state is $E^{(0)} \approx -13.6\text{eV}$. When an H^- ion is formed by adding a second electron, the true total energy for the two electrons is larger than $2E^{(0)}$. What is the main reason for this difference?

   The main reason for this is energy difference is the repulsive Coulombic interaction between the two electrons.

   A detailed explanation:

   The new total Hamiltonian is comprised of two single electron Hamiltonians as above (1, 2) and their repulsive Coulomb interactions.

   $$H_{H-} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}},$$

   Given the repulsive potential perturbation, the energy (up to the first order corrections) should be:

   $$E_{tot}^{(1)} = E^{(0)} + E^{(0)} + \langle\psi^{(0)}\left|\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right|\psi^{(0)}\rangle > 2E^{(0)}.$$

(c) Write an expression for the perturbation responsible for the deviation from $2E^{(0)}$ in (b).

The Hamiltonian term responsible for this deviation is

$$\frac{e^2}{4\pi\varepsilon_0 r_{12}},$$

the energy deviation (to the first order) is

$$\langle\psi^{(0)}\left|\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right|\psi^{(0)}\rangle.$$

(d) A variational calculation is performed to approximate the best ground state energy of H^-. A trial wavefunction $\phi_{\text{trial}}(Z_{eff};\vec{r}_1,\vec{r}_2)$ is defined, where Z_{eff} is a parameter describing the effective nuclear charge and $\vec{r}_1,\vec{r}_2$ are the coordinate vectors of the two electrons. An expression for the energy is found as

$$\begin{aligned} E(Z_{eff}) &= \frac{\langle\phi_{\text{trial}}|\hat{H}|\phi_{\text{trial}}\rangle}{\langle\phi_{\text{trial}}|\phi_{\text{trial}}\rangle} \\ &= \left[Z_{eff}^2 - \frac{7}{4}Z_{eff}\right]V, \end{aligned}$$

where V is a constant. What value for Z_{eff} gives the best estimate for the true ground state energy?

To find the optimal Z_{eff} that minimizes the trial energy expectation, we set the derivative of $E(Z_{eff})$ w.r.t. Z_{eff} to 0.

$$\begin{aligned} \frac{dE(Z_{eff})}{dZ_{eff}} = 2Z_{eff} - \frac{7}{4} &= 0 \\ \therefore Z_{eff} &= \frac{7}{8}. \end{aligned}$$

(e) Explain why or why not an optimal value of the effective nuclear charge $Z_{eff} < 1$ would make physical sense for the H^- ion.

This makes sense since each electron experiences a screened (or shielded) nuclear charge due to the presence of the other electron. This screening (or shielding) lowers the **effective** nuclear charge from the actual H^- ion nuclear charge of 1.

4. 30 pts - **Spin-$\frac{1}{2}$ particle in a magnetic field**

A spin-$\frac{1}{2}$ particle (e.g., an electron) is placed in a uniform magnetic field of strength B pointing in the z-direction. The magnetic moment operators in the x and z direction are related to the spin operators via:

$$\hat{\mu}_x = \gamma \hat{s}_x = \gamma \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{1}$$

$$\hat{\mu}_z = \gamma \hat{s}_z = \gamma \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{2}$$

The Hamiltonian of the system is given by:

$$\hat{H} = -\hat{\mu}_z B = -\gamma \hat{s}_z B = -\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3}$$

(a) Show that $\hat{H}$ commutes with $\hat{s}_z$, i.e., $[\hat{H}, \hat{s}_z] = 0$. Justify your answer using matrix commutators. Explain in a few words why the energy of the particle depends on the orientation of its spin.

Since the Hamiltonian can be written as

$$\hat{H} = -\gamma B \hat{s}_z,$$

the commutator $[\hat{H}, \hat{s}_z]$ is given by

$$[\hat{H}, \hat{s}_z] = \hat{H}\hat{s}_z - \hat{s}_z\hat{H}.$$

Substituting $\hat{H} = -\gamma B \hat{s}_z$ into the commutator, we obtain

$$[\hat{H}, \hat{s}_z] = (-\gamma B \hat{s}_z)\hat{s}_z - \hat{s}_z(-\gamma B \hat{s}_z) = -\gamma B(\hat{s}_z^2 - \hat{s}_z^2) = 0.$$

Alternatively, noting that both $\hat{H}$ and $\hat{s}_z$ are diagonal matrices:

$$\hat{H} = -\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\begin{aligned}
\hat{H}\hat{s}_z - \hat{s}_z\hat{H} &= \left(-\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \left(\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) - \left(\frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \left(-\frac{\gamma \hbar B}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \\
&= -\frac{\gamma \hbar^2 B}{4} \left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \\
&= -\frac{\gamma \hbar^2 B}{4} \left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right] = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}.
\end{aligned}$$

Thus, we have shown that $\hat{H}$ commutes with $\hat{s}_z$.Since the total energy $\hat{H} = -\hat{\mu}_z B = -\gamma \hat{s}_z B$ depends on the spin operator $\hat{s}_z$, the eigenstates of $\hat{s}_z$ will corresponds to two different energies of the particle. Thus, when the spin is aligned with the magnetic field (i.e., $s_z = +\hbar/2$), the energy is lower; Conversely, when the spin is anti-aligned with the magnetic field (i.e., $s_z = -\hbar/2$), the energy is higher

(b) Do $\hat{H}$ and $\hat{s}_x$ commute? Justify your answer using matrix commutators.

$$\hat{H} = -\frac{\gamma\hbar B}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \quad \hat{s}_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.$$

First, compute $\hat{H}\hat{s}_x$:

$$\hat{H}\hat{s}_x = -\frac{\gamma\hbar^2 B}{4}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} = -\frac{\gamma\hbar^2 B}{4}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}.$$

Compute $\hat{s}_x\hat{H}$:

$$\hat{s}_x\hat{H} = -\frac{\gamma\hbar^2 B}{4}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = -\frac{\gamma\hbar^2 B}{4}\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}.$$

This simplifies to

$$[\hat{H}, \hat{s}_x] = -\frac{\gamma\hbar^2 B}{4}\left[\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix} - \begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}\right] = -\frac{\gamma\hbar^2 B}{4}\begin{pmatrix}0 & 2\\ -2 & 0\end{pmatrix}.$$

Therefore, $\hat{H}$ and $\hat{s}_x$ do not commute.
We can also use the algebraic method noting

$$[\hat{s}_z, \hat{s}_x] = i\hbar\, \hat{s}_y.$$

Since the Hamiltonian is given by

$$\hat{H} = -\frac{\gamma B}{2}\,\hat{s}_z,$$

its commutator with $\hat{s}_x$ is

$$[\hat{H}, \hat{s}_x] = -\frac{\gamma B}{2}\,[\hat{s}_z, \hat{s}_x] = -\frac{\gamma B}{2}\,(i\hbar\, s_y) = -i\frac{\gamma B}{2}\,\hat{s}_y.$$

Because $-i\gamma\hbar B/2\,\hat{s}_y \neq 0$, we conclude that $\hat{H}$ and $\hat{s}_x$ do not commute.

(c) What are the eigenvalues and normalized eigenvectors of $\hat{H}$? The Hamiltonian is given by

$$\hat{H} = -\frac{\gamma\hbar B}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

To find the eigenvalues, we solve the eigenvalue equation

$$\det\left(\hat{H} - \lambda I\right) = 0.$$

Substituting $\hat{H}$ we have:

$$\det\left(-\frac{\gamma\hbar B}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} - \lambda\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\right) = \det\begin{pmatrix}-\frac{\gamma\hbar B}{2} - \lambda & 0\\ 0 & \frac{\gamma\hbar B}{2} - \lambda\end{pmatrix} = 0.$$

Solving these, we obtain the following eigenvalues:

$$\lambda_1 = -\frac{\gamma\hbar B}{2} \quad \text{and} \quad \lambda_2 = \frac{\gamma\hbar B}{2}.$$

The corresponding eigenvectors are obtained by noticing that $\hat{H}$ is already diagonal. Therefore, the eigenvectors corresponding to λ_1 and λ_2 are:

$$\mathbf{v}_1 = \begin{pmatrix}1\\ 0\end{pmatrix} \quad \text{for} \quad \lambda_1 = -\frac{\gamma\hbar B}{2},$$

$$\mathbf{v}_2 = \begin{pmatrix}0\\ 1\end{pmatrix} \quad \text{for} \quad \lambda_2 = \frac{\gamma\hbar B}{2}.$$