University of Illinois at Chicago
Department of Physics

Quantum Mechanics
Qualifying Examination

9:00 am – 12:00 pm
**Question 1**

In heavy (large $Z$) hydrogen-like atoms, where to a very good approximation the reduced mass $\mu$ is equal to the electron mass $m_e$, relativistic corrections to the electron’s kinetic energy need to be taken into account due to its large orbital velocity.

a) Show that the first-order relativistic correction to the electron’s kinetic energy is given by $\hat{H}_1 = -\frac{1}{2m_e c^2} \left( \frac{p^2}{2m_e} \right)^2$.

b) Verify that $\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0}$ for the 1s state of the hydrogen-like atom.

c) Similarly, show that $\left\langle \frac{1}{r^2} \right\rangle = \frac{2Z^2}{a_0^2}$ for the 1s state of the hydrogen-like atom.

d) Using the fact that the unperturbed Hamiltonian, $\hat{H}_0 = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$, and the results from parts (a), (b) and (c), evaluate the first-order perturbation due to the relativistic correction to the electron’s kinetic energy.
(1) a) Since \( E = \sqrt{p^2c^2 + m_e^2c^4} = K + m_e^2c^2 \), where \( K \) is the kinetic energy,

\[
\Rightarrow K = \sqrt{p^2c^2 + m_e^2c^4} - m_e^2c^2 = m_e^2c^2 \sqrt{1 + \frac{p^2c^2}{2m_e^2c^4}} - m_e^2c^2
\]

\[
\approx m_e^2c^2 \left( 1 + \frac{p^2c^2}{2m_e^2c^4} - \frac{1}{8} \left( \frac{p^2c^2}{m_e^2c^4} \right)^2 + \ldots \right) - m_e^2c^2
\]

\[
\approx \frac{p^2c^2}{2m_e^2c^4} - \frac{1}{8} \frac{p^4c^4}{m_e^2c^8} \Rightarrow \frac{p^2c^2}{2m_e^2c^4} - \frac{1}{2m_e^2c^4} \left( \frac{p^2c^2}{2m_e^2c^4} \right)^2
\]

\[\text{\textit{First-order correction}} \quad \Delta H_1 = -\frac{1}{2m_e^2c^4} \left( \frac{p^2c^2}{2m_e^2c^4} \right)^2\]

b) Since \( \langle \hat{r} | \phi_{100} \rangle = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-2Zr/a_0} \), we have

\[
\langle \frac{1}{r} \rangle = \int_0^\infty r^2 dr \cdot \frac{1}{r} \cdot 4 \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0}
\]

\[
= 4 \left( \frac{Z}{a_0} \right)^3 \int_0^\infty dr \cdot r e^{-2Zr/a_0} = 4 \left( \frac{Z}{a_0} \right)^3 \frac{a_0^2}{4Z^2}
\]

\[\Rightarrow \langle \frac{1}{r} \rangle = \frac{Z}{a_0}\]
c) Similarly \( \langle \frac{1}{r^2} \rangle \) for \( \langle r \mid \phi_{100} \rangle \) is given by

\[
\langle \frac{1}{r^2} \rangle = \int_0^\infty r^2 dr \cdot \frac{1}{r^2} \cdot 4 \left( \frac{\mathbf{r}^2}{a_0} \right)^3 e^{-2\mathbf{r}/a_0}
\]

\[
= 4 \left( \frac{\mathbf{r}}{a_0} \right)^3 \left[ -\frac{a_0}{2\mathbf{r} e} - \frac{2\mathbf{r}/a_0}{2\mathbf{r} e} \right]_0
\]

\[
= 2 \left( \frac{\mathbf{r}}{a_0} \right)^2
\]

\[\Box\]

d) As \( \mathbf{H}_0 = \frac{p^2}{2m_e} - \frac{2e^2}{4\pi\varepsilon_0 r} \), we have

\[
\hat{\mathbf{H}}_1 = -\frac{1}{2me^2} \left( \frac{\mathbf{p}^2}{2me} \right)^2 = -\frac{1}{2me^2} \left( \hat{\mathbf{H}}_0 + \frac{2e}{4\pi\varepsilon_0 r} \right)^2
\]

\[\Rightarrow \langle \phi_{100} \mid \hat{\mathbf{H}}_1 \mid \phi_{100} \rangle \]

\[= -\frac{1}{2me^2} \langle \phi_{100} \mid \hat{\mathbf{H}}_0^2 + 2\hat{\mathbf{H}}_0 \frac{2e}{4\pi\varepsilon_0 r} + \left( \frac{2e}{4\pi\varepsilon_0 r} \right)^2 \rangle \phi_{100} \rangle
\]

\[= -\frac{1}{2me^2} \left[ \frac{E_{100}^2}{2} + \frac{2eE_{100}}{2\pi}\frac{1}{r} + \left( \frac{2e}{4\pi\varepsilon_0} \right)^2 \langle \frac{1}{r^2} \rangle \right]
\]

\[E_{100} = -13.6 \, \frac{Z^2}{eV}
\]
\( E_{100} = - \frac{m_e}{2h^2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \), \( \langle \frac{1}{r} \rangle = \frac{2}{a_0} \) and \( \langle \frac{1}{r^2} \rangle = 2 \left( \frac{2}{a_0} \right)^2 \) with \( a_0 = \frac{4\pi\epsilon_0 h^2}{m_e e^2} \), we have

\[
\langle \phi_{100}^* \hat{H} \phi_{100} \rangle = -\frac{1}{2m_e c^2} \left( \frac{m_e^2 e^4}{h^4 \epsilon_0^4} \right) \left[ \frac{1}{64} - \frac{1}{16} + \frac{1}{8} \right]
\]

\[
= -\frac{5m_e^2 e^4}{128 c^2 h^4 \epsilon_0^4}
\]

\[
= -\frac{5}{2m_e c^2} \left( E_{100} \right)^2
\]
Consider an attractive delta-function potential \(-\Lambda \delta(x)\), where the parameter \(\Lambda\) characterizes the strength of the delta-function, positioned at the center of an infinite square well of width \(2a\); that is, a potential given by

\[
\begin{align*}
V(x < -a) &= \infty \\
V(-a < x < 0) &= 0 \\
V(x = 0) &= -\Lambda \delta(x) \\
V(0 < x < a) &= 0 \\
V(x > a) &= \infty
\end{align*}
\]

a) Show that the equation determining the energy \(E\) of the eigenstate bound to the delta-function is given by

\[
\tanh(\kappa a) = \frac{\hbar^2 \kappa}{m \Lambda},
\]

where \(\hbar \kappa = \sqrt{2m|E|}\) and \(m\) is the mass of the particle.

b) What is the minimum strength of the delta-function for which a state with \(E < 0\) exists?
\( \psi_1 = A e^{Kx} - e^{-Kx} \)
\( \psi_2 = C e^{Kx} + D e^{-Kx} \)
\( K = \sqrt{\frac{2m|E|}{\hbar^2}} \)

Boundary conditions at \( x = \pm a \) give
\( \psi_1(a) = 0 = Ae^{Ka} - e^{-Ka} \implies A = -Be^{-2Ka} \quad \text{...1} \)
\( \psi_2(-a) = 0 = Ce^{-Ka} + De^{Ka} \implies C = -De^{2Ka} \quad \text{...2} \)

Boundary conditions at the \( S \)-function give
\( \psi_1(0) = \psi_2(0) \implies A + B = C + D \quad \text{...3} \)
\( \frac{\partial \psi_1}{\partial x} \bigg|_{x=0} - \frac{\partial \psi_2}{\partial x} \bigg|_{x=0} = -\frac{2mE}{\hbar^2} \psi(0) \)
\( \implies K(A - B) - K(C - D) = -\frac{2mE}{\hbar^2} (A + B) \quad \text{...4} \)

Inserting 1 and 2 into 3 and 4 to eliminate \( A \) and \( NC \) gives
(2) a) contd.

\[
B(1 - e^{-2Ka}) = D(1 - e^{2Ka}) \\
- KB(1 + e^{-2Ka}) + KD(1 + e^{2Ka}) = \frac{-2mL}{h^2} B(1 - e^{-2Ka})
\]

\[
\Rightarrow -K(1 + e^{-2Ka}) + K(1 + e^{2Ka})(1 - e^{-2Ka}) = \frac{-2mL}{h^2} (1 - e^{-2Ka})
\]

\[
\Rightarrow 2K \cosh(Ka) = \frac{2mL}{h^2} \sinh(Ka)
\]

\[
\Rightarrow \tanh(Ka) = \frac{h^2K}{mL}
\]

b) For a state with \( E < 0 \) to exist, the above equation must have a solution, other than at \( K = 0 \). This means that

\[
\frac{d}{dK} \left( \tanh(Ka) \right) > \frac{h^2}{mL} \quad \text{at} \quad K = 0
\]

\[
\Rightarrow a > \frac{h^2}{mL}
\]
\[ b) \text{cont.} \]

So, \( L > \frac{h^2}{ma} \) in for state with \( E < 0 \).

Graphically, this is self-evident:

\[ \text{initial gradient } a \]

\[ \text{tanh}(Ka) \]

\[ \frac{L \cdot \frac{h^2}{m} K}{m \cdot L} \]
Question 3

Quantum dots are important material systems in nanoscience.

Consider an electron of charge $e$ and mass $m_e$ confined in an idealized quantum dot with $V(r) = 0$ for $r < a$ and $V(r) = \infty$ for $r > a$; that is, an infinite spherical well of radius $a$. The eigenstates of this potential are given by

$$\langle \mathbf{r} | \psi_{nlm} \rangle = C_{nl} j_l \left( \frac{s_{nl} r}{a} \right) Y_{lm}(\theta, \phi),$$

where $Y_{lm}(\theta, \phi)$ is the spherical harmonic associated with the usual angular momentum quantum numbers $l$ and $m$, and $C_{nl}$ is the normalization constant for the $l$th spherical Bessel function $j_l$ with roots $s_{nl}$. The first three spherical Bessel functions with $\rho = s_{nl} r / a$ are

$$j_0(\rho) = \frac{\sin \rho}{\rho}, \quad j_1(\rho) = \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho}, \quad j_2(\rho) = \left( \frac{3}{\rho^3} - \frac{1}{\rho^2} \right) \sin \rho - \frac{3}{\rho^2} \cos \rho,$$

and the first few roots are given below:

<table>
<thead>
<tr>
<th>$s_{nl}$</th>
<th>$l = 0$</th>
<th>$l = 1$</th>
<th>$l = 2$</th>
<th>$l = 3$</th>
<th>$l = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$</td>
<td>$\pi$</td>
<td>4.49</td>
<td>5.76</td>
<td>6.99</td>
<td>9.36</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>$2\pi$</td>
<td>7.73</td>
<td>9.10</td>
<td>10.42</td>
<td></td>
</tr>
<tr>
<td>$n = 3$</td>
<td>$3\pi$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The spherical Bessel functions also satisfy the relation

$$\int_0^a r^2 dr j_l \left( \frac{s_{nl} r}{a} \right) j_l \left( \frac{s_{nl'} r}{a} \right) = \frac{a^2}{2} [j_{l-1}(s_{nl})]^2 \delta_{nn'}.$$

a) What are the energies of the lowest four eigenstates?

b) Evaluate the normalization constants $C_{10}$ and $C_{11}$.

c) Consider the state $\langle \mathbf{r} | \psi \rangle = A \left[ \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho} \right] \sin \theta \cos \phi + \frac{\sin \rho}{\rho}$, where $A$ is a constant.

With what probability is the ground state energy measured? And what is the probability of measuring a $z$-component of the angular momentum with a value $+\hbar$?

d) In the presence of a strong homogeneous magnetic field $\mathbf{B}$, the energy states split – the Zeeman effect. Neglecting spin (the normal Zeeman effect), the additional contribution to the Hamiltonian can be written as $H_I = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B}$. Amongst the four lowest states identified in part (a), at what magnetic field strength will states originating from one energy level overlap energetically with those from another?
a) Since the states are given as \( j \neq (k_{\text{rel}} r) \) with 
\( k_{\text{rel}} = \frac{s_{\text{rel}}}{a} \), the wave vector, the state energies will be 

\[
E_{n\ell} = \frac{k_{\text{rel}}^2 \hbar^2}{2m_e} = \frac{\hbar^2 s_{\text{rel}}^2}{2ma^2}
\]

Hence, the first 4 are:

\[n = 1, \ell = 0: E_{10} = \frac{\pi^2 \hbar^2}{2ma^2} = 4.93\left(\frac{\hbar^2}{ma^2}\right) \text{ ... ground state} \]

\[n = 1, \ell = 1: E_{11} = 10.08\left(\frac{\hbar^2}{ma^2}\right) \]

\[n = 1, \ell = 2: E_{12} = 16.95\left(\frac{\hbar^2}{ma^2}\right) \]

\[n = 2, \ell = 0: E_{20} = \frac{4\pi^2 \hbar^2}{2ma^2} = 19.74\left(\frac{\hbar^2}{ma^2}\right) \]

b) Since the \( Y_m \) are already normalized, we need only evaluate the integral

\[
1 = |C_{n\ell}|^2 \int_0^a r^2 dr \left| j_e\left(\frac{s_{\text{rel}} r}{a}\right) \right|^2
\]
(3) b) cont. For \( C_{10} \): \( 1 = |C_{10}|^2 \int_0^a r^2dr \frac{\sin^2(\pi r/a)}{(\pi r/a)^2} = |C_{10}|^2 \frac{a^3}{2\pi^2} \)

\[ \Rightarrow C_{10} = \frac{\pi}{a} \sqrt{\frac{2}{a}} = \frac{4.443}{a} \]

For \( C_{11} \): \( 1 = |C_{11}|^2 \int_0^a r^2dr \frac{j_1^2(s_{11}r/a)}{s_{11}^2} = \frac{a^3}{2} \left[ j_0(s_{11}) \right]^2 \)

Using given relation.

Now; \( j_0(s_{11}) = \frac{\sin(4.49)}{4.49} = -0.217 \)

\[ \Rightarrow C_{11} = \frac{6.51}{a^{1.5}} \]

c) \( \psi = A \left[ \left( \frac{\sin^2 \theta - \cos^2 \theta}{\phi^2 / \gamma} \right) \sin \theta \cos \phi + \frac{\sin \theta}{\phi} \right] \)

\[ \frac{j_1(s_{11}r/a)}{j_0(s_{11}r/a)} \]

\[ \frac{1}{2} \sin \theta \left( e^{i\phi} + e^{-i\phi} \right) \]

\[ = \frac{1}{2a^{3/2}} \left( Y_{11} - Y_{11}^\dagger \right) \]
3c) cont'd

So, we clearly have

$$\Psi = \alpha C_{11} j_1 \left( \frac{s_{11} r}{a} \right) (Y_1 - Y_{11}) + \beta C_{10} j_0 \left( \frac{s_{10} r}{a} \right) Y_{10}$$

with

$$\alpha = \sqrt{\frac{8\pi}{3}} \cdot \frac{A}{C} \quad \beta = \sqrt{\frac{4\pi}{C_{10}}}$$

$$\lim_{r \to \infty} \Psi = \Psi_{\infty} \neq 0$$

Now, we also know that $2|\alpha|^2 + |\beta|^2 = 1$, thus

$$1 = \frac{8\pi}{6} \frac{A^2}{C_{11}} + 4\pi \frac{A^2}{C_{10}^2} = 4\pi \frac{A^2}{C_{10}^2} \left( \frac{1}{C_{11}^2} + \frac{1}{C_{10}^2} \right)$$

$$\Rightarrow A = \frac{1.165}{a^{1/4} a^{1/4}} \quad \text{from part (b)}$$

$$\bullet$$ Probability of measuring $E_{10}$, $|\beta|^2 = \frac{4\pi A^2}{C_{10}^2} = 0.866$

$$\bullet$$ Probability of measuring $E_{11}$, $|\alpha|^2 = \frac{2\pi A^2}{3 C_{11}^2} = 0.067$
Both $l=0$ states do not split, but the $l=1$ and $l=2$ states do. Since the energy gap between the ground state $E_{10}$ and $E_{11}$ is roughly equal to that between $E_{11}$ and $E_{12}$, we expect the $l=1$ and $l=2$ states to be involved.

\[ H_1 = \frac{e}{2m_e} \vec{B} \cdot \vec{L} \]

\[ = \frac{eB}{2m_e} \vec{L} \cdot \vec{z} \]

\[ \Rightarrow \Delta E = \frac{ekB}{2m_e} \]

\[ B = 0 \quad B \neq 0 \]

So, states overlap when

\[ E_{21} - E_{11} = 3\Delta E = \frac{3e\hbar B}{2m_e} = 6.51 \frac{\hbar^2}{m_e a^2} \]

\[ \Rightarrow B = 4.34 \frac{\hbar}{ea^2} \]
Question 4

Field emission, a quantum tunneling phenomenon, occurs when a DC electric field $E_{\text{DC}}$ applied perpendicular to a material surface becomes sufficiently strong to allow electrons in the material to tunnel out into the vacuum.

![Diagram of potential barrier with tunneling electron](image)

In materials like metals, the zero-point energy $E$ of the electrons in the metal is usually defined in terms of the Fermi energy $\varepsilon_F$ (the energy of the last filled electronic state at zero Kelvin), which is located at an energy $\Phi$ (the material work function) below the vacuum energy.

a) Using the approximation for the one-dimensional tunneling probability through a ‘thick’ barrier,

$$|T|^2 \approx \exp \left[ -2 \int_a^b dx \sqrt{\frac{2m}{\hbar^2}} (V(x) - E) \right],$$

of thickness $b - a$, determine the transmission probability for an electron at an arbitrary energy $E'$; that is, at an energy $E' = \varepsilon_F + \Phi - E$ below the top of the barrier.

b) In a real material at non-zero temperature $T$, the energy distribution of electrons is given by the Fermi function

$$f(E) = \frac{1}{1 + \exp \left( -\frac{\varepsilon_F - E}{k_B T} \right)},$$

where $k_B$ is Boltzmann’s constant. For $\exp[(\Phi - E')/k_B T] >> 1$, determine the energy below the top of the barrier for which electron field emission is most probable.
To evaluate $|T|^2 \propto \exp \left[ -2 \int_a^b dx \sqrt{\frac{2m}{\hbar^2}} \left( V(x) - E \right) \right]$, we need to determine $V(x)$ in the $a \rightarrow b$ interval and find $a$ and $b$ (the integral limits). Using $x = 0$ at the metal surface, we have

$$V(x) = E_F + \Phi - eE_{DC} x$$

$$V(x_0) = E = E_F + \Phi - eE_{DC} x_0 \implies x_0 = \frac{E_F + \Phi - E}{eE_{DC}}$$

$$|T|^2 \propto \exp \left[ -2 \int_0^{x_0} dx \sqrt{\frac{2m}{\hbar^2}} \left( E_F + \Phi - eE_{DC} x - E \right) \right]$$

$$= \exp \left[ -2 \sqrt{\frac{2meE_{DC}}{\hbar^2}} \int_0^{x_0} dx \sqrt{x_0 - x} \right]$$

$$\geq \frac{2}{3} \left( \frac{E_F + \Phi - E}{eE_{DC}} \right)^{3/2}$$
Hence,
\[ |T|^2 \propto \exp \left[ - \frac{4\sqrt{2m}}{3e\hbar E_{pc}} (\varepsilon_F + \Phi - E)^{3/2} \right] \]

b) Including the Fermi distribution, we expect the transmission probability at energy \( E \) to be
\[ |T(E)|^2 \propto \frac{\exp \left[ - \alpha (\varepsilon_F + \Phi - E)^{3/2} \right]}{1 + \exp \left[ \beta (E - \varepsilon_F) \right]} \]

with \( \alpha = \frac{4\sqrt{2m}}{3e\hbar E_{pc}} \) and \( \beta = \frac{1}{k_B T} \).

So, the most probable emission is at
\[ \frac{\partial}{\partial E} |T(E)|^2 = 0 \]
\[ \Rightarrow - \frac{3\alpha}{2} (\varepsilon_F + \Phi - E)^{1/2} \left( 1 + e^{-\beta (E - \varepsilon_F)} \right)^{-1} - \beta e^{-\beta (E - \varepsilon_F)} = 0 \]

But since \( E' = \varepsilon_F + \Phi - E \Rightarrow E - E_F = \Phi - E' \) and \( \exp \left[ (\Phi - E')/k_B T \right] \gg 1 \), we get...
\[ -\frac{3x}{2} \sqrt{E_{\text{max}}'} = \beta \]

\[ E_{\text{max}}' = \frac{4\beta^2}{9x^2} = \frac{e^2 h^2}{8mk_{\beta}^2 T^2} \]

...the energy below the top of the barrier for most probable field emission.

\[ T(E_{\text{max}}') \approx \exp \left[-\frac{e^2 h E_{\text{mc}}}{12mk_{\beta}^3 T^3}\right] \]

as a result of (b).
Question 5

Consider the following \textit{spatial-coordinate-independent} two-particle Hamiltonian for a spin system

\[ \hat{H} = A + BS_1 \cdot S_2 , \]

where \(A\) and \(B\) are constants. Calculate the eigenstates and eigenvalues of \(\hat{H}\) for two identical spin \(\frac{1}{2}\) particles

a) using the uncoupled basis, matrices, and spinors, and
b) using the coupled basis.

Consider the following \textit{spatial-coordinate-independent} two-particle Hamiltonian for a spin system consisting of two identical spin \(\frac{1}{2}\) particles:

\[ \hat{H} = A + BS_1 \cdot S_2 \]

where \(A\) and \(B\) are constants.

a) Find the \(4 \times 4\) matrix representation of \(\hat{H}\) in the uncoupled basis set

\[
|\uparrow\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix},
|\uparrow\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix},
|\downarrow\uparrow\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix},
\text{ and } |\downarrow\downarrow\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix},
\]

where \(|\uparrow\rangle\) represents a spin-up particle with \(S_z = \frac{1}{2}\hbar\) and a spin-down particle with \(S_z = -\frac{1}{2}\hbar\) is \(|\downarrow\rangle\).

b) Calculate the eigenvalues of \(\hat{H}\).

c) What are the eigenstates of the diagonalized Hamiltonian?

d) Verify your results by finding the eigenvalues of the four states in the coupled basis \(|S,M\rangle\) representing the total spin \(S\) and its \(z\)-component \(M\).
a) Since \( \hat{S}_x \hat{S}_z = \hat{S}_z \hat{S}_x + \hat{S}_y \hat{S}_z + \hat{S}_z \hat{S}_y \) and \( \hat{S}_z = \hat{S}_x \pm i \hat{S}_y \), we have

\[
\hat{H} = A + B \hat{S}_z, \quad \hat{S}_z = A + \frac{1}{2} B \hat{S}_z + \frac{1}{2} B \hat{S}_z + B \hat{S}_z \hat{S}_z
\]

\[
\begin{array}{c|cccc}
\hat{H} & |\uparrow\uparrow> & |\uparrow\downarrow> & |\downarrow\uparrow> & |\downarrow\downarrow> \\
|\uparrow\uparrow> & A + \frac{1}{4} B t^2 & 0 & 0 & 0 \\
|\uparrow\downarrow> & 0 & A - \frac{1}{4} B t^2 & \frac{1}{2} B t^2 & 0 \\
|\downarrow\uparrow> & 0 & \frac{1}{2} B t^2 & A - \frac{1}{4} B t^2 & 0 \\
|\downarrow\downarrow> & 0 & 0 & 0 & A + \frac{1}{4} B t^2 \\
\end{array}
\]

\[
\text{since } \hat{S}_z |\uparrow> = \frac{t}{\sqrt{2}} |\uparrow> \quad \hat{S}_z |\downarrow> = -\frac{t}{\sqrt{2}} |\downarrow>, \\
\hat{S}_z |\uparrow\downarrow> = \hat{S}_z |\downarrow\uparrow> = 0, \quad \hat{S}_z |\uparrow\uparrow> = \frac{t}{2} |\uparrow\uparrow>, \quad \hat{S}_z |\downarrow\downarrow> = \frac{t}{2} |\downarrow\downarrow>,
\]

and \( \hat{S}_z |\uparrow\downarrow> = \frac{t}{\sqrt{2}} |\uparrow\uparrow> \).

b) Clearly \( |\uparrow\uparrow> \) and \( |\downarrow\downarrow> \) are already eigenstates of \( \hat{H} \) with eigenvalues \( A + \frac{1}{4} B t^2 \). The central 2×2 block can be diagonalized to find the other two eigenvalues:

\[
\begin{vmatrix}
A - \frac{1}{4} B t^2 - \lambda & \frac{1}{2} B t^2 \\
\frac{1}{2} B t^2 & A - \frac{1}{4} B t^2 - \lambda
\end{vmatrix} = 0
\]

\[
\Rightarrow (A - \frac{1}{4} B t^2 - \lambda)^2 - \frac{1}{4} B^2 t^4 = 0
\]

\[
\Rightarrow A - \frac{1}{4} B t^2 - \lambda = \pm \frac{1}{2} B t^2
\]
(5) b) centd. \[ \lambda = A + \frac{1}{2} B t^2 \]

and \[ \lambda = A - \frac{3}{4} B t^2 \]

\[ \frac{1}{2} B t^2 \left( \begin{array}{cc} -1 & 1 \\ 1 & -1 \end{array} \right) \left( \begin{array}{c} a \\ b \end{array} \right) = 0 \quad \Rightarrow \quad a = b \]

so Eigenstate is \[ \frac{1}{\sqrt{2}} \left( |1b\rangle + |b\rangle \right) \]

For \[ \lambda = A - \frac{3}{4} B t^2 \], we get

\[ \frac{1}{2} B t^2 \left( \begin{array}{cc} 1 & 1 \\ 1 & -1 \end{array} \right) \left( \begin{array}{c} a \\ b \end{array} \right) = 0 \quad \Rightarrow \quad a = -b \]

so Eigenstate is \[ \frac{1}{\sqrt{2}} \left( |1b\rangle - |b\rangle \right) \]

And the other two eigenstates for \[ \lambda = A + \frac{1}{4} B t^2 \] are \[ |1b\rangle \] and \[ |b\rangle \].

d) In the coupled basis \[ |S, M\rangle \]

\[ \hat{H} = A + B \hat{S}_1 \cdot \hat{S}_2 = A + \frac{1}{2} B \left( \hat{S}_1^2 - \hat{S}_2^2 \right) \]
Thus, the energy eigenvalues are

\[ E = A + \frac{1}{2} B \left( 2 \frac{t^2}{4} - \frac{3 t^2}{4} - \frac{3 t^2}{4} \right) = A + \frac{1}{4} B t^2 \quad \text{for } S = 1 \]

\[ E = A + \frac{1}{2} B \left( 0 - \frac{3 t^2}{4} - \frac{3 t^2}{4} \right) = A - \frac{3}{4} B t^2 \quad \text{for } S = 0 \]

Consequently, since the coupled basis are \( |S=1, M\rangle \) and \( |S=0, 0\rangle \), we have

\[
\begin{align*}
\text{Eigenstates} & \quad \text{Eigenvalues} \\
|S=1, M=1\rangle & \quad A + \frac{1}{4} B t^2 \\
|S=1, M=0\rangle & \\
|S=1, M=-1\rangle & \\
|S=0, M=0\rangle & A - \frac{3}{4} B t^2
\end{align*}
\]

In agreement with prior parts of question.
Equation Sheet

\[ Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta \quad Y_{11}(\theta, \phi) = \pm \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin \theta \]

\[ Y_{20}(\theta, \phi) = \frac{5}{\sqrt{16\pi}} (3 \cos^2 \theta - 1) \quad Y_{21}(\theta, \phi) = \pm \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \sin \theta \cos \theta \]

\[ Y_{2\pm 2}(\theta, \phi) = \frac{15}{32\pi} e^{\pm 2i\phi} \sin^2 \theta \]

\[ E_n = \left[ \frac{\mu}{2\hbar^2} \left( \frac{Ze^2}{4\pi \varepsilon_0} \right)^2 \right] \frac{1}{n^2} = -13.6 \frac{Z}{n^2} \text{ eV} \quad a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{\mu e^2} \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M_{\text{nucleus}}} \]

\[ R_{10}(r) = 2 \left( \frac{Z}{a_0} \right)^3 \exp \left[ -\frac{Zr}{a_0} \right] \quad R_{20}(r) = 2 \left( \frac{Z}{2a_0} \right)^3 \left( 1 - \frac{Zr}{2a_0} \right) \exp \left[ -\frac{Zr}{2a_0} \right] \]

\[ R_{21}(r) = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^3 \frac{Zr}{a_0} \exp \left[ -\frac{Zr}{2a_0} \right] \]

\[ \int_0^\infty dx \ x^n \exp(-ax^2) = \frac{\Gamma\left(\frac{m+1}{2}\right)}{2a^{(m+1)/2}} \quad \Gamma(n + 1) = n\Gamma(n), \Gamma(n + 1) = n!, \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \]

so that \[ \int_0^\infty dx \ x^{2n} \exp(-\lambda^2 x^2) = \frac{1.3.5... (2n+1) \sqrt{\pi}}{2^n \lambda^{2n+1}} \]

\[ \int_0^\infty dx \ x^n \ e^{-\lambda x} = \frac{n!}{\lambda^{n+1}} \]

\[ \int dx \sqrt{A + Bx} = \frac{2}{3B} (A + Bx)^{3/2} \quad \int dx \ x \sqrt{A + Bx} = -\frac{2(2A - 3Bx)(A + Bx)^{3/2}}{15B^2} \]