University of Illinois at Chicago
Department of Physics

Quantum Mechanics
Qualifying Examination

January 4, 2010.
9:00 am – 12:00 pm

Question 1

In heavy (large Z) hydrogen-like atoms, where to a very good approximation the reduced mass μ 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 $\hat{H}_1 = -\frac{1}{2m_e c^2}\left(\frac{\mathbf{p}^2}{2m_e}\right)^2$.

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, $\hat{H}_0 = \frac{\mathbf{p}^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$, 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 $E = \sqrt{p^2c^2 + m_e^2c^4} = K + m_ec^2$, where K is the kinetic energy

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

$$\simeq m_ec^2\left(1 + \frac{p^2}{2m_e^2c^2} - \frac{1}{8}\left(\frac{p^2}{m_e^2c^2}\right)^2 + \cdots\right) - m_ec^2$$

$$\cong \frac{p^2}{2m_e} - \frac{1}{8}\frac{p^4}{m_e^3c^2} = \frac{p^2}{2m_e} - \frac{1}{2m_ec^2}\left(\frac{p^2}{2m_e}\right)^2$$

$\therefore$ First-order correction $\underline{\underline{\hat{H}_1 = -\frac{1}{2m_ec^2}\left(\frac{p^2}{2m_e}\right)^2}}$

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

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

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

$$\therefore \underline{\underline{\left\langle \frac{1}{r}\right\rangle = \frac{Z}{a_0}}}$$

(1) c) Similarly $\langle \frac{1}{r^2} \rangle$ for $\langle r | \phi_{100} \rangle$ is given by

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

$$= 4 \left(\frac{Z}{a_0}\right)^3 \left[-\frac{a_0}{2Z} e^{-2Zr/a_0} \right]_0^\infty$$

$$\therefore \underline{\underline{\langle \frac{1}{r^2} \rangle = 2 \left(\frac{Z}{a_0}\right)^2}}$$

d) As $\hat{H}_0 = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$, we have

$$\hat{H}_1 = -\frac{1}{2m_e c^2} \left(\frac{p^2}{2m_e}\right)^2 = -\frac{1}{2m_e c^2} \left(\hat{H}_0 + \frac{Ze}{4\pi\epsilon_0 r} \right)^2$$

$$\Rightarrow \langle \phi_{100} | \hat{H}_1 | \phi_{100} \rangle$$

$$= -\frac{1}{2m_e c^2} \langle \phi_{100} | \hat{H}_0^2 + 2\hat{H}_0 \frac{Ze}{4\pi\epsilon_0 r} + \left(\frac{Ze}{4\pi\epsilon_0 r}\right)^2 | \phi_{100} \rangle$$

$$= -\frac{1}{2m_e c^2} \left[E_{100}^2 + \frac{ZeE_{100}}{2\pi\epsilon_0} \langle \frac{1}{r} \rangle + \left(\frac{Ze}{4\pi\epsilon_0}\right)^2 \langle \frac{1}{r^2} \rangle \right]$$

$\ldots E_{100} = -13.6 Z^2 \text{ eV}$

① d) contd.

Since $E_{100} = -\frac{m_e}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)$, $\langle\frac{1}{r}\rangle = \frac{Z}{a_0}$ and

$\langle\frac{1}{r^2}\rangle = 2\left(\frac{Z}{a_0}\right)^2$ with $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$, we have

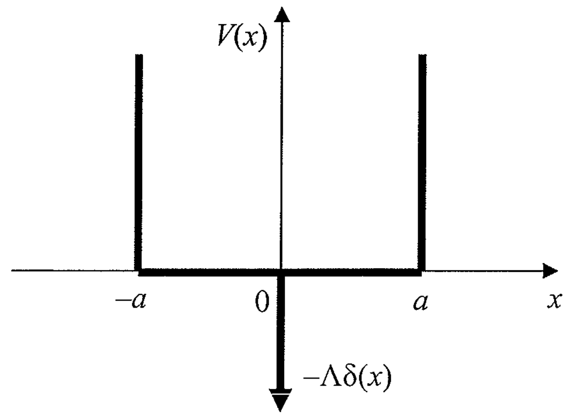
$$\langle\phi_{100}|\hat{H}_1|\phi_{100}\rangle = -\frac{1}{2m_e c^2}\left(\frac{m_e^2 Z^4 e^8}{h^4 \epsilon_0^4}\right)\left[\frac{1}{64} - \frac{1}{16} + \frac{1}{8}\right]$$

$$= -\frac{5 m_e Z^4 e^8}{128 c^2 \hbar^4 \epsilon_0}$$

$$= -\frac{5}{2m_e c^2}\left(E_{100}\right)^2$$

Question 2

Consider an *attractive* delta-function potential $-\Lambda\delta(x)$, where the parameter Λ 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



$V(x < -a) = \infty$
$V(-a < x < 0) = 0$
$V(x = 0) = -\Lambda\delta(x)$
$V(0 < x < a) = 0$
$V(x > a) = \infty$

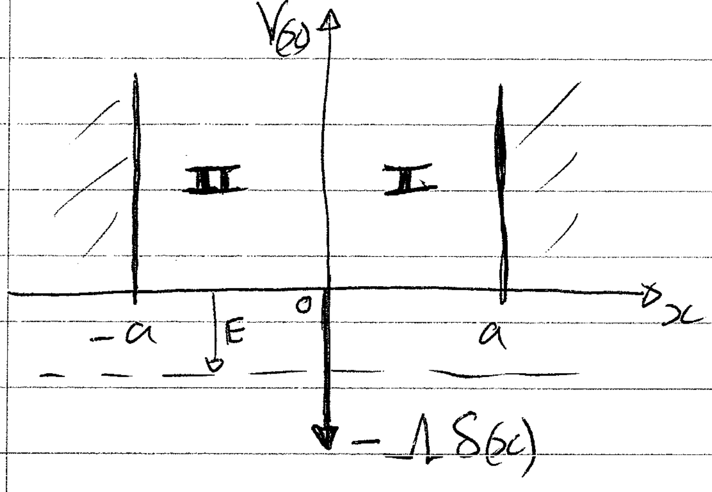
a) Show that the equation determining the energy E of the eigenstate bound to the delta-function is given by

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

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?

② a)



$$\psi_I = Ae^{Kx} + Be^{-Kx}$$

$$\psi_{II} = Ce^{Kx} + De^{-Kx}$$

$$K = \sqrt{\frac{2m|E|}{\hbar^2}}$$

Boundary conditions at $x = \pm a$ give

$$\psi_I(a) = 0 = Ae^{Ka} + Be^{-Ka} \Rightarrow A = -Be^{-2Ka} \quad \ldots (1)$$

$$\psi_{II}(-a) = 0 = Ce^{-Ka} + De^{Ka} \Rightarrow C = -De^{+2Ka} \quad \ldots (2)$$

Boundary conditions at the δ-function give

$$\psi_I(0) = \psi_{II}(0) \Rightarrow A + B = C + D \quad \ldots (3)$$

$$\left.\frac{\partial \psi_I}{\partial x}\right|_{x=0} - \left.\frac{\partial \psi_{II}}{\partial x}\right|_{x=0} = \frac{-2m\Lambda}{\hbar^2}\psi(0)$$

$$\Rightarrow K(A-B) - K(C-D) = -\frac{2m\Lambda}{\hbar^2}(A+B) \quad \ldots (4)$$

Inserting (1) and (2) into (3) and (4) to eliminate A and C gives

2 a) contd.

$$B\left(1-e^{-2Ka}\right) = D\left(1-e^{2Ka}\right)$$

$$-KB\left(1+e^{-2Ka}\right) + KD\left(1+e^{2Ka}\right) = -\frac{2m\Lambda}{\hbar^2} B\left(1-e^{-2Ka}\right)$$

$$\Rightarrow -K\left(1+e^{-2Ka}\right) + \frac{K\left(1+e^{2Ka}\right)\left(1-e^{-2Ka}\right)}{\left(1-e^{2Ka}\right)} = -\frac{2m\Lambda}{\hbar^2}\left(1-e^{-2Ka}\right)$$

$$\Rightarrow 2K\cosh(Ka) = \frac{2m\Lambda}{\hbar^2}\sinh(Ka)$$

$$\therefore \tanh(Ka) = \frac{\hbar^2 K}{m\Lambda}$$

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

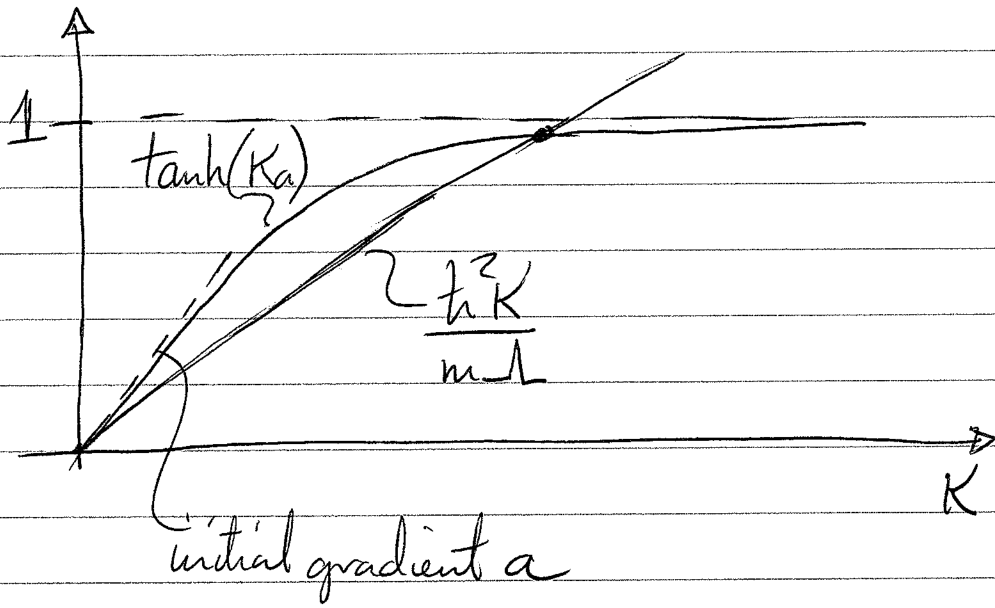
$$\frac{\partial}{\partial K}\left(\tanh(Ka)\right) > \frac{\hbar^2}{m\Lambda} \quad @ \ K=0$$

$$\Rightarrow a > \frac{\hbar^2}{m\Lambda}$$

2 b) contd.

So, $\Lambda \geqslant \dfrac{\hbar^2}{ma}$ for state with $E<0$.

Graphically, this is self-evident:



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

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

and the first few roots are given below:

s_{nl}	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
$n = 1$	π	4.49	5.76	6.99	9.36
$n = 2$	2π	7.73	9.10	10.42	
$n = 3$	3π				

The spherical Bessel functions also satisfy the relation

$$\int_0^a r^2 dr\, j_l\left(\frac{s_{nl} r}{a}\right) j_l\left(\frac{s_{n'l} r}{a}\right) = \frac{a^3}{2}\left[j_{l-1}(s_{nl})\right]^2 \delta_{nn'} .$$

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

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

c) Consider the state $\langle \mathbf{r} | \psi \rangle = A\left[\left(\frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}\right)\sin\theta\cos\phi + \frac{\sin\rho}{\rho}\right]$, 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 $H_1 = \frac{e}{2m_e}\mathbf{L} . \mathbf{B}$. 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?

③ a) Since the states are given as $j_\ell(k_{n\ell}r)$ with $k_{n\ell} = s_{n\ell}/a$, the wave vector, the state energies will be

$$E_{n\ell} = \frac{k_{n\ell}^2 \hbar^2}{2m_e} = \frac{\hbar^2 s_{n\ell}^2}{2m_e a^2}$$

Hence, the first 4 are:

$$n=1,\ \ell=0 \ : \ E_{10} = \frac{\pi^2\hbar^2}{2m_e a^2} = 4.93\left(\frac{\hbar^2}{m_e a^2}\right) \quad \text{... ground state}$$

$$n=1,\ \ell=1 \ : \ E_{11} = 10.08\left(\frac{\hbar^2}{m_e a^2}\right)$$

$$n=1,\ \ell=2 \ : \ E_{12} = 16.95\left(\frac{\hbar^2}{m_e a^2}\right)$$

$$n=2,\ \ell=0 \ : \ E_{20} = \frac{4\pi^2\hbar^2}{2m_e a^2} = 19.74\left(\frac{\hbar^2}{m_e a^2}\right)$$

b) Since the $Y_{\ell m}$ are already normalized, we need only evaluate the integral

$$1 = |C_{n\ell}|^2 \int_0^a r^2 dr \left| j_\ell\left(\frac{s_{n\ell} r}{a}\right)\right|^2$$

(3) b) contd. For C_{10}: $1 = |C_{10}|^2 \int_0^a r^2 dr \frac{\sin^2\left(\frac{\pi r}{a}\right)}{\left(\frac{\pi r}{a}\right)^2} = |C_{10}|^2 \frac{a^3}{2\pi^2}$

$$\Rightarrow \underline{\underline{C_{10} = \frac{\pi}{a}\sqrt{\frac{2}{a}} = \frac{4.443}{a\sqrt{a}}}}$$

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

... using given relation.

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

$$\Rightarrow \underline{\underline{C_{11} = \frac{6.51}{a\sqrt{a}}}}$$

c) $$\psi = A\left[\underbrace{\left(\frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}\right)}_{j_1\left(\frac{s_{11} r}{a}\right)} \underbrace{\sin\theta\cos\phi}_{} + \underbrace{\frac{\sin\rho}{\rho}}_{j_0\left(\frac{s_{10} r}{a}\right)}\right]$$

$$\sin\theta\cos\phi = \frac{1}{2}\sin\theta.\left(e^{i\phi} + e^{-i\phi}\right)$$

$$= \frac{1}{2}\sqrt{\frac{8\pi}{3}}\left(Y_{1-1} - Y_{11}\right)$$

(3) c) contd

So, we clearly have

$$\psi = \alpha C_{11} j_1\left(\frac{s_{11} r}{a}\right)\left(Y_{1-1} - Y_{11}\right) + \beta C_{10} j_0\left(\frac{s_{10} r}{a}\right) Y_{00}$$

with

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

as $1 = \sqrt{4\pi}\, Y_{00}$.

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

$$1 = \frac{8\pi}{6}\frac{A^2}{C_{11}^2} + 4\pi\frac{A^2}{C_{10}^2} = 4\pi A^2\left(\frac{1}{3C_{11}^2} + \frac{1}{C_{10}^2}\right)$$

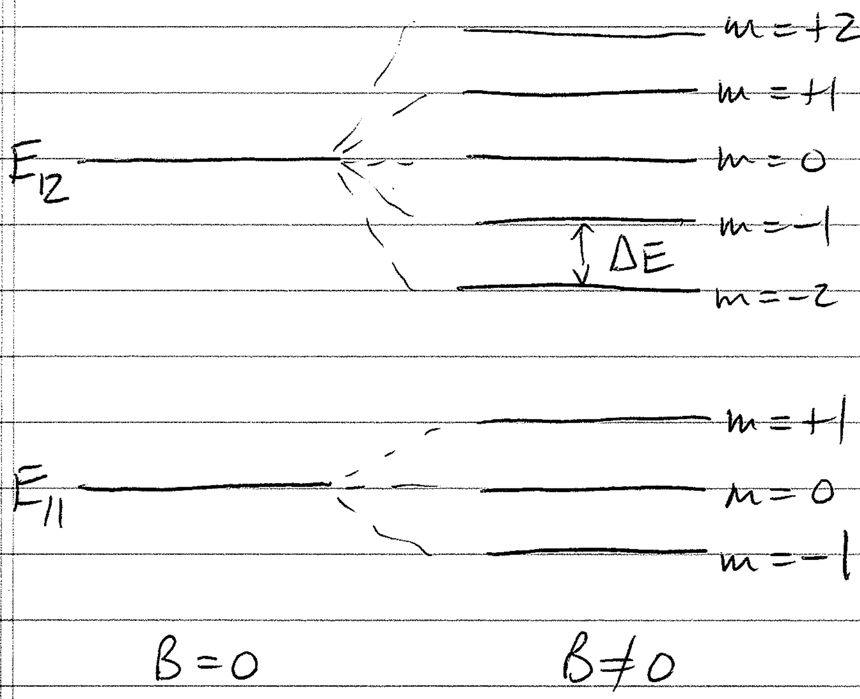
$$\Rightarrow A = \frac{1.165}{a\sqrt{a}} \quad \text{from part (b)}$$

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

$\therefore$ Probability of measuring $L_z = +\hbar$, $|\alpha|^2 = \frac{2\pi A^3}{3C_{11}^2} = \underline{\underline{0.067}}$

(3) d) contd.

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;



$$\hat{H}_1 = \frac{e}{2m_e}\vec{B}.\vec{L}$$

$$= \frac{eB}{2m_e}\hat{L}_z$$

$$\Rightarrow \Delta E = \frac{e\hbar}{2m_e}B$$

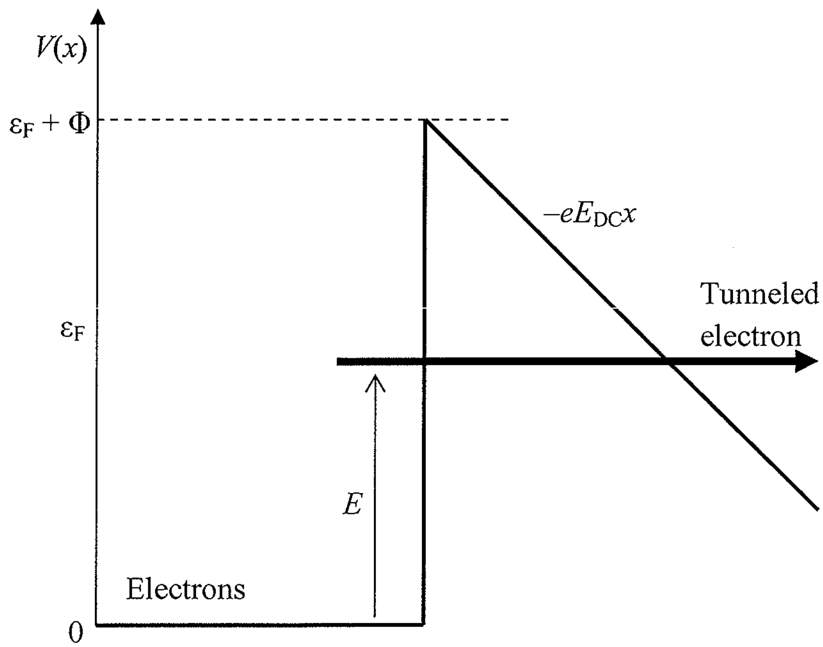
So, states over-lap when

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

$$\Rightarrow B = 4.34\frac{\hbar}{ea^2}$$

Question 4

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



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

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

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

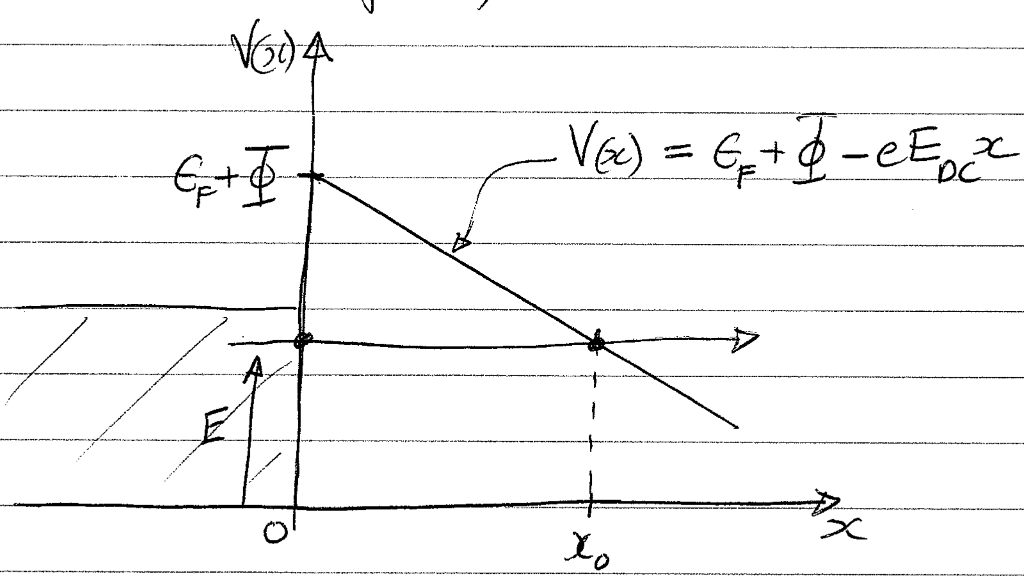
of thickness $b - a$, determine the transmission probability for an electron at an arbitrary energy E; that is, at an energy $E' = \varepsilon_F + \Phi - E$ below the top of the barrier.

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.

(4) a) To evaluate $|T|^2 \simeq \exp\left[-2\int_a^b dx \sqrt{\frac{2m}{\hbar^2}(V(x)-E)}\right]$, we need to determine $V(x)$ in the $a \to b$ interval and find a and b (the integral limits). Using $x=0$ at the metal surface, we have



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

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

$$= \exp\left[-2\sqrt{\frac{2meE_{DC}}{\hbar^2}}\underbrace{\int_0^{x_0} dx \sqrt{x_0 - x}}_{\frac{2}{3}\left(\frac{\epsilon_F+\Phi-E}{eE_{DC}}\right)^{3/2}}\right]$$

(4) a) contd.

Hence,

$$|T|^2 \simeq \exp\left[-\frac{4\sqrt{2m}}{3e\hbar E_{DC}}\left(\epsilon_F+\Phi-E\right)^{3/2}\right]$$

b) Including the Fermi distribution, we expect the transmission probability at energy E to be

$$|T(E)|^2 \simeq \frac{\exp\left[-\alpha\left(\epsilon_F+\Phi-E\right)^{3/2}\right]}{1+\exp\left[\beta(E-\epsilon_F)\right]}$$

... with $\alpha = \dfrac{4\sqrt{2m}}{3e\hbar E_{DC}}$ and $\beta = \dfrac{1}{k_B T}$.

So, the most probable emission is at

$$\frac{\partial}{\partial E}|T(E)|^2 = 0$$

$$\Rightarrow -\frac{3\alpha}{2}\left(\epsilon_F+\Phi-E\right)^{1/2}\left(1+e^{\beta(E-\epsilon_F)}\right)-\beta e^{\beta(E-\epsilon_F)} = 0$$

But, since $E' = \epsilon_F+\Phi-E \Rightarrow E-\epsilon_F = \Phi - E'$ and $\exp\left[(\Phi-E')/k_BT\right] \gg 1$, we get

④ b) cont'd.

$$-\frac{3\alpha}{2}\sqrt{E'_{max}} = \beta$$

$$\Rightarrow E'_{max} = \frac{4\beta^2}{9\alpha^2} = \underline{\underline{\frac{e^2\hbar^2 E_{DC}^2}{8mk_\beta^2 T^2}}}$$

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

[NOTE:

$$|T(E'_{max})|^2 \simeq \exp\left[-\frac{e^2\hbar^2 E_{DC}^2}{12mk_\beta^3 T^3}\right]$$

as a result of (b).]

Question 5

Consider the following *spatial-coordinate-independent* two-particle Hamiltonian for a spin system

$$\hat{H} = A + B\mathbf{S}_1.\mathbf{S}_2 \ ,$$

where A and B are constants. Calculate the eigenstates and eigenvalues of $\hat{H}$ for two *identical* spin ½ particles

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

Consider the following *spatial-coordinate-independent* two-particle Hamiltonian for a spin system consisting of two *identical* spin ½ particles:

$$\hat{H} = A + B\mathbf{S}_1.\mathbf{S}_2$$

where A and B are constants.

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

$$\left|\uparrow\uparrow\right\rangle = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \left|\uparrow\downarrow\right\rangle = \begin{pmatrix}0\\1\\0\\0\end{pmatrix}, \left|\downarrow\uparrow\right\rangle = \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \text{ and } \left|\downarrow\downarrow\right\rangle = \begin{pmatrix}0\\0\\0\\1\end{pmatrix},$$

where $\left|\uparrow\right\rangle$ 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 $\left|\downarrow\right\rangle$.

b) Calculate the eigenvalues of $\hat{H}$.
c) What bare the eigenstates of the diagonalized Hamiltonian?
d) Verify your results by finding the eigenvalues of the four states in the coupled basis $\left|S,M\right\rangle$ representing the total spin S and its z-component M.

5) a) Since $\hat{S}_1 \cdot \hat{S}_2 = \hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}$ and $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$, we have

$$\hat{H} = A + B\hat{S}_1\cdot\hat{S}_2 = A + \tfrac{1}{2}B\hat{S}_{1+}\hat{S}_{2-} + \tfrac{1}{2}B\hat{S}_{1-}\hat{S}_{1+} + B\hat{S}_{1z}\hat{S}_{2z}$$

$\Rightarrow$

$\hat{H}$	$\lvert\uparrow\uparrow\rangle$	$\lvert\uparrow\downarrow\rangle$	$\lvert\downarrow\uparrow\rangle$	$\lvert\downarrow\downarrow\rangle$
$\lvert\uparrow\uparrow\rangle$	$A+\frac{1}{4}B\hbar^2$	0	0	0
$\lvert\uparrow\downarrow\rangle$	0	$A-\frac{1}{4}B\hbar^2$	$\frac{1}{2}B\hbar^2$	0
$\lvert\downarrow\uparrow\rangle$	0	$\frac{1}{2}B\hbar^2$	$A-\frac{1}{4}B\hbar^2$	0
$\lvert\downarrow\downarrow\rangle$	0	0	0	$A+\frac{1}{4}B\hbar^2$

... since $\hat{S}_z|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle$, $\hat{S}_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle$, $\hat{S}_+|\uparrow\rangle = \hat{S}_-|\downarrow\rangle = 0$, $\hat{S}_+|\downarrow\rangle = \hbar|\uparrow\rangle$, and $\hat{S}_-|\uparrow\rangle = \hbar|\downarrow\rangle$.

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

$$\begin{vmatrix} A-\frac{1}{4}B\hbar^2-\lambda & \frac{1}{2}B\hbar^2 \\ \frac{1}{2}B\hbar^2 & A-\frac{1}{4}B\hbar^2-\lambda \end{vmatrix} = 0$$

$$\Rightarrow \left(A-\tfrac{1}{4}B\hbar^2-\lambda\right)^2 - \tfrac{1}{4}B^2\hbar^4 = 0$$

$$\Rightarrow A - \tfrac{1}{4}B\hbar^2 - \lambda = \pm\tfrac{1}{2}B\hbar^2$$

(5) b) contd. $\therefore$ Eigenvalues are $\lambda = \underline{\underline{A + \frac{1}{4} B\hbar^2}}$

and $\lambda = \underline{\underline{A - \frac{3}{4} B\hbar^2}}$

c) For $\lambda = A + \frac{1}{2} B\hbar^2$, we have for the central 2x2 block

$$\frac{1}{2} B\hbar^2 \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \quad \Rightarrow \quad a = b$$

$\therefore$ Eigenstate is $\underline{\underline{\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)}}$

For $\lambda = A - \frac{3}{4} B\hbar^2$, we get

$$\frac{1}{2} B\hbar^2 \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \quad \Rightarrow \quad a = -b$$

$\therefore$ Eigenstate is $\underline{\underline{\frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)}}$

And the other two eigenstates for $\lambda = A + \frac{1}{4} B\hbar^2$ are $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$.

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

$$\hat{H} = A + B \hat{S}_1 \cdot \hat{S}_2 = A + \frac{1}{2} B \left(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2 \right)$$

⑤ d) contd.

Thus, the energy eigenvalues are

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

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

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

$$\text{Eigenstates} \left\{ \begin{array}{l} \left.\begin{array}{l} |S=1, M=1\rangle \\ |S=1, M=0\rangle \\ |S=1, M=-1\rangle \end{array}\right\} A + \frac{1}{4}B\hbar^2 \\ \\ |S=0, M=0\rangle \quad A - \frac{3}{4}B\hbar^2 \end{array} \right\} \text{Eigenvalues}$$

... in agreement with prior parts of question.

Equation Sheet

$$Y_{00}(\theta,\phi)=\frac{1}{\sqrt{4\pi}} \qquad Y_{10}(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{1\pm1}(\theta,\phi)=\mp\sqrt{\frac{3}{8\pi}}\,e^{\pm i\phi}\sin\theta$$

$$Y_{20}(\theta,\phi)=\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right) \qquad Y_{2\pm1}(\theta,\phi)=\mp\sqrt{\frac{15}{8\pi}}\,e^{\pm i\phi}\sin\theta\cos\theta$$

$$Y_{2\pm2}(\theta,\phi)=\sqrt{\frac{15}{32\pi}}\,e^{\pm 2i\phi}\sin^2\theta$$

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

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

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

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

$$\text{so that} \quad \int_0^\infty dx\,x^{2n}\exp\left(-\lambda^2x^2\right)=\frac{1.3.5\ldots(2n+1)\sqrt{\pi}}{2^n\lambda^{2n+1}}$$

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

$$\int dx\sqrt{A+Bx}=\frac{2}{3B}(A+Bx)^{\frac{3}{2}} \qquad \int dx\,x\sqrt{A+Bx}=-\frac{2(2A-3Bx)(A+Bx)^{3/2}}{15B^2}$$