Chem 332

Assignment #2

(due Monday, February 1st, in class)

Q1. **a)** A free electron in a 0.15 Tesla magnetic field drops from higher to lower magnetic potential energy and emits a photon. Calculate the wavelength of the photon.

b) In what region of electromagnetic spectrum (radio, microwave, infrared, visible, ultraviolet) is the emitted photon?

[4] **c)** Give a definition of the SI unit the **Tesla**.

d) Who is the Tesla unit named after? (*10 points deducted if you mention Elon Musk.*)

Hints: The magnetic potential energy of a free electron in a magnetic field of strength B is

$$V_{\text{magnetic}} = m_s g_e \beta_0 B$$

m_s is the electron spin magnetic quantum number (± ½), $g_e = 2.0023$ is the anomalous spin factor (from the Dirac equation), and β_0 is the Bohr magneton (9.274×10^{-24} J T^{-1}).

Q2. **a)** Give a brief (< 50 words) description of **electron spin resonance (ESR) spectroscopy.**

b) Why is ESR spectroscopy especially useful for studies of **free radicals**?

[4] **c)** ESR spectroscopy is also called **electron paramagnetic resonance (EPR) spectroscopy**. Why? (Explain the meaning of "paramagnetic".)

d) ESR spectroscopy is analogous to NMR spectroscopy. Explain briefly.

Q3. Approximate numerical methods, such as perturbation and variational calculations, are
[1] essential for studies of quantum chemistry. Why?

Q4. To illustrate perturbation (successive-approximation) calculations, suppose you need to solve the equation $x^2 = 10$ for x (the square root of 10) without using a calculator.

Start with the initial "zero-order" approximation $x_0 = 3$, which gives $x_0^2 = 9$, a close *exact* solution to the equation to be solved. Use Δx_1 for the correction to x_0 and multiply out:

$$(x_0 + \Delta x_1)^2 = x_0^2 + 2x_0\Delta x_1 + (\Delta x_1)^2 = 10$$

[2] Omitting the second-order term $(\Delta x_1)^2$ (the second-order product of two hopefully small first-order corrections, and therefore even smaller) gives

$$x_0^2 + 2x_0\Delta x_1 = 10$$

a) Use this equation to calculate the first-order perturbation correction Δx_1 and the first-order approximation $x_0 + \Delta x_1$ for the square root of 10.

b) Repeat ("iterate") the calculation in **a** using the first-order approximation $x_0 + \Delta x_1$ to calculate a more accurate approximation for the square root of 10.

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Q5. We used **perturbation theory** to calculate the magnetic potential energy of a hydrogen
[1] atom in a magnetic field, *without realizing it*! Give $\hat{H}^{(1)}$ and $\Delta E^{(1)}$ for this system.

Q6. A particle of mass m is trapped in a one-dimensional box extending from $x = 0$ to $x = L$. The potential energy inside the box is zero: $V(x) = 0 \qquad (0 < x < L)$

Solving the Schrodinger equation $\hat{H}^{(0)}\psi^{(0)}(x) = E^{(0)}\psi^{(0)}(x)$ for this system gives the
[2] exact wave function $\psi^{(0)}$ and the exact energy $E^{(0)}$:

$$\psi^{(0)}(x) = \sqrt{2/L}\sin(\pi x/L) \qquad\qquad E^{(0)} = h^2/8mL^2$$

Suppose the system is perturbed by providing the potential energy $V(x) = b$ (a constant) to the left-side of the box. Calculate the **first-order perturbation $\Delta E^{(1)}$** to the energy.

Hints: $\hat{H}^{(0)} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$ and $\hat{H}^{(1)} = b \quad (\text{for } 0 < x < L/2)$

Q7. This question refers to a particle of mass m in a box extending from $x = 0$ to $x = L$ with zero potential energy inside the box. To illustrate **variational calculations**, we'll use

$$\varphi(x) = Cx(L - x)$$

as a trial ("*guessed*") wave function describing the particle. (C is a constant.)

a) Show the trial wave function obeys the required boundary conditions:

$$\varphi(0) = 0 \qquad\qquad \varphi(L) = 0$$

[6]

b) Derive an expression for the variational energy $\dfrac{\int \varphi^* \hat{H}\varphi\, dx}{\int \varphi^* \varphi\, dx}$ of the particle.

c) Show the variational energy calculated in part **b** obeys the variational theorem

$$E_{\text{variational}} \geq E_{\text{actual}}$$

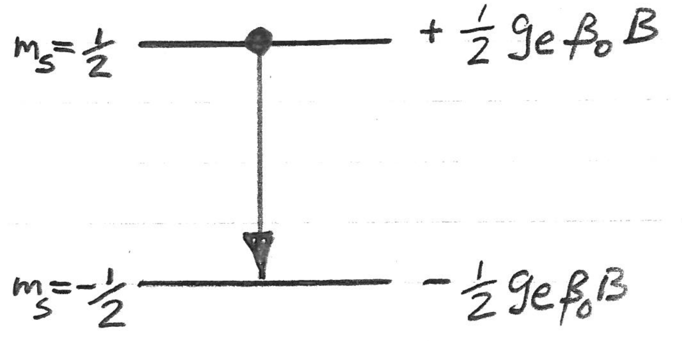
Hint: the actual ground-state energy of the particle (see Question 6) is $h^2/8mL^2$.

d) Evaluate the variational constant C in terms of L.

Chem 332 **Assignment #2**

Q1 a) The magnetic potential energy of a free electron in an externally-applied magnetic field (strength B) is

$$V_{magnetic} = m_S g_e \beta_0 B$$



$$\Delta E = h\nu$$
$$= \frac{1}{2} g_e \beta_0 B - \left(-\frac{1}{2} g_e \beta_0 B\right)$$
$$= g_e \beta_0 B$$

$$\Delta E = 2.0023\,(9.274 \times 10^{-24}\ \mathrm{J\,T^{-1}})(0.15\ \mathrm{T})$$
$$\boxed{\Delta E = 2.78 \times 10^{-24}\ \mathrm{J}}$$

$\nu = \Delta E / h = 4.20 \times 10^{6}\ \mathrm{s^{-1}}$ (frequency)

b) $\lambda = \frac{c}{\nu} = \boxed{0.0713\ \mathrm{m}}$ $\boxed{\text{microwave region}}$
(1 mm to 1 m wavelengths)

c) an electric charge of one Coulomb (C) moving at right angles to a magnetic field of one Tesla experiences a force of magnitude one Newton

$$1\ \mathrm{T} = \boxed{\frac{\mathrm{kg}}{\mathrm{C\,s}}}$$

d) American genius electrical engineer (1856–1943) who made important advances in AC circuits, electric motors, and radio communications

Ⓠ2 electron spin resonance (ESR) spectroscopy

a) radiation (usually microwaves) absorbed by samples in "resonance" (matching the energy difference) with changes in spin magnetic potential energy of electrons which depend on the chemical environment of the electrons

b) free radicals have unpaired electrons and therefore non-zero spin magnetic moments to interact with an applied magnetic field and produce strong ESR absorbances

(no spin magnetic moment for paired electrons (magnetic dipoles for $m_s = -\frac{1}{2}$, $m_s = \frac{1}{2}$ cancel)

c) electron paramagnetic resonance spectroscopy (EPR)

why "paramagnetic"?

the applied magnetic field causes the electron spin magnetic moments to align parallel to the field

d) NMR spectroscopy to measure changes in the spin magnetic potential of nuclei which are also sensitive to chemical environments

Q3 the Schrodinger equation $\hat{H}\psi = E\psi$ can not be solved "exactly" ("analytically") for atoms and molecules with more than two particles (He, Li, Be, ... and all molecules)

numerical methods are therefore essential for quantum chemistry

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Q4 solve $x^2 = 10$ for the square root of 10

a) "guess" $x_0 = 3$ and calculate the first-order correction $\Delta x_1^{(1)}$ to x to give a better estimate of $\sqrt{10}$

$$(x_0 + \Delta x^{(1)})^2 = x_0^2 + 2x_0\Delta x^{(1)} + (\Delta x^{(1)})^2 = 10$$

ignore this small 2nd-order term

$$x_0^2 + 2x_0\Delta x^{(1)} \approx 10 \qquad \Delta x^{(1)} = \frac{10 - x_0^2}{2x_0}$$

$$\Delta x^{(1)} = \frac{10 - 3^2}{2(3)} = \frac{1}{6}$$

"zero-order" estimate of $\sqrt{10}$ is $x_0 = 3$ ← (5 % error in x_0 because $\sqrt{10} = 3.1622\ldots$)

with "first-order" correction $\Delta x^{(1)}$:

$$x^{(0)} + \Delta x^{(1)} = \boxed{3 + \frac{1}{6} = 3.1666..}$$ ← (only a −0.14% error in $\sqrt{10}$!)

(Q4 cont.)

b) for an even more accurate estimate of $\sqrt{10}$, repeat part a using $3\frac{1}{6}$ as x_0

$$x_0^2 + 2x_0\Delta x^{(1)} \approx 10$$

$$\left(3\tfrac{1}{6}\right)^2 + 2\left(3\tfrac{1}{6}\right)\Delta x_1^{(1)} = 10$$

gives $\Delta x^{(1)} = -0.00438596\ldots$

and $x_0 + \Delta x^{(1)} = 3\frac{1}{6} - 0.00438596\ldots$

$$= \boxed{3.1622807\ldots} \leftarrow \left(\begin{array}{c}\text{only a}\\ -0.000096\,\%\\ \text{error in } \sqrt{10}\end{array}\right)$$

Q5 Zeeman effect for the hydrogen atom

perturbation Hamiltonian for the magnetic potential energy:

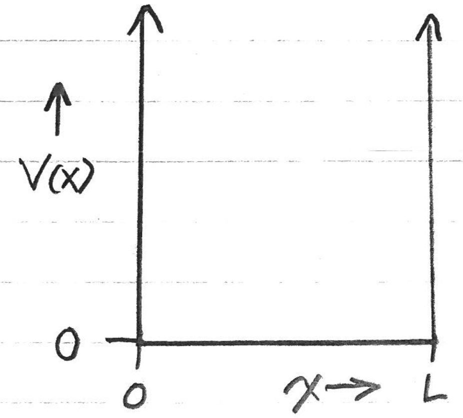
$$\hat{V}_{magnetic} = V_{magnetic} = \hat{H}^{(1)} = \frac{em\hbar}{2m_e}B_z$$

first-order perturbation to the energy of the atom:

$$\Delta E^{(1)} = \frac{e\hbar}{2m_e}\, m B_z = \beta_0 m B_z \qquad m = 0, \pm 1, \pm 2, \ldots \pm l$$

First-Order Perturbation Calculation

Ⓠ⑥ ground-state particle in a box

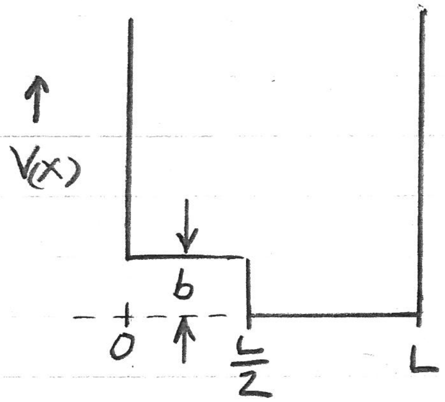


$$\psi^{(0)}_{(x)} = \sqrt{\frac{2}{L}}\ \sin\left(\frac{\pi x}{L}\right) \quad \text{(exact)}$$

$$E^{(0)} = \frac{h^2}{8mL^2} \quad \text{(exact)}$$

$$\hat{H}^{(0)} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$

"perturbed" particle in a box:



perturbation Hamiltonian:

$$\hat{H}^{(1)} = b \quad \text{for } 0 < x < \frac{L}{2}$$

(left side of the box)

perturbation energy (first order)
$$\Delta E^{(1)} = \int_0^L \psi^{(0)*}_{(x)}\, \hat{H}^{(1)}\, \psi^{(0)}_{(x)}\, dx$$

$$= \int_0^{L/2} \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\, b\, \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right) dx$$

$$\Delta E^{(1)} = b\,\frac{2}{L}\int_0^{L/2}\sin^2\left(\frac{\pi x}{L}\right) dx$$

$$\left(\frac{2}{L}\int_0^L \sin^2\left(\frac{\pi x}{L}\right) dx = 1 \quad \text{(normalized } \psi^{(0)}_{(x)}\text{)} \quad \text{so } \frac{2}{L}\int_0^{L/2}\sin^2\left(\frac{\pi x}{L}\right) dx = \frac{1}{2}\right)$$

$$\boxed{\Delta E^{(1)} = \frac{b}{2}}$$

makes sense! (particle spends "half the time" on the left side with potential energy b)

Variational Calculation

Q7 particle in a box between 0 and L

"guess" the trial wave function $\varphi(x) = Cx(L-x)$

a) $\varphi(x=0) = C(0)(L-0) = 0$

$\varphi(x=L) = C(L)(L-L) = 0$

b) variational energy $E' = \dfrac{\int_0^L \varphi^*(x)\,\hat{H}\,\varphi(x)\,dx}{\int_0^L \varphi^*(x)\,\varphi(x)\,dx}$

$$\int_0^L \varphi^*(x)\,\hat{H}\,\varphi(x)\,dx = \int_0^L Cx(L-x)\left(-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\right)Cx(L-x)\,dx$$

$$= -\frac{h^2}{8\pi^2 m}C^2\int_0^L x(L-x)\overset{=-2}{\boxed{\frac{d^2}{dx^2}(Lx-x^2)}}\,dx$$

$$= -\frac{h^2}{8\pi^2 m}C^2(-2)\int_0^L x(L-x)\,dx$$

$$= 2\frac{h^2}{8\pi^2 m}C^2\int_0^L (xL-x^2)\,dx = 2\frac{h^2}{8\pi^2 m}C^2\left(\frac{Lx^2}{2}-\frac{x^3}{3}\right)\Bigg|_0^L$$

$$= 2\frac{h^2}{8\pi^2 m}C^2\left(\frac{L^3}{2}-\frac{L^3}{3}\right) = 2\frac{h^2}{8\pi^2 m}C^2\frac{L^3}{6}$$

$$= \frac{C^2L^5}{3\pi^2}\,\frac{h^2}{8mL^2}$$

(Q7 b cont.)

$$\int_0^L \varphi^*(x)\,\varphi(x)\,dx = \int_0^L C\,x(L-x)\,C\,x(L-x)\,dx$$

$$= C^2\int_0^L x^2(L-x)^2\,dx$$

$$= C^2\int_0^L (L^2x^2 - 2Lx^3 + x^4)\,dx$$

$$= C^2\left[\frac{L^2x^3}{3}\Big|_0^L - 2L\,\frac{x^4}{4}\Big|_0^L + \frac{x^5}{5}\Big|_0^L\right]$$

$$= C^2\left(\frac{L^5}{3} - \frac{1}{2}L^5 + \frac{L^5}{5}\right)$$

$$= \frac{C^2L^5}{30}$$

variational energy $E' = \dfrac{\int_0^L \varphi^*(x)\,\hat{H}\,\varphi(x)\,dx}{\int_0^L \varphi^*(x)\,\varphi(x)\,dx} = \dfrac{\frac{C^2L^5}{3\pi^2}\,\frac{h^2}{8mL^2}}{\frac{C^2L^5}{30}}$

$$\boxed{E' = \frac{10}{\pi^2}\,\frac{h^2}{8mL^2}} = \frac{10}{\pi^2}\,E_{exact}$$

c) $E' = (1.0132\ldots)\dfrac{h^2}{8mL^2} = (1.0132\ldots)$(exact energy of the particle)

$E' > E_{exact}$ by $1.32\ldots\%$ variation theorem is obeyed

d) evaluate the variational parameter C

φ(x) must be normalized:

$$\int_0^L \varphi(x)^* \varphi(x)\,dx = 1 = \frac{C^2 L^5}{30}$$

$$\boxed{C = \sqrt{\frac{30}{L^5}}}$$

at $x = \frac{L}{2}$ (half-way across the box):

$$\varphi\left(x = \frac{L}{2}\right) = C\frac{L}{2}\left(L - \frac{L}{2}\right) = C\frac{L^2}{4}$$

$$= \sqrt{\frac{30}{L^5}}\;\frac{L^2}{4} = \sqrt{\frac{30/16}{L}} = \sqrt{\frac{30}{2(16)}}\sqrt{\frac{2}{L}}$$

$$= \sqrt{\frac{15}{16}}\sqrt{\frac{2}{L}} = 0.9682\ldots\sqrt{\frac{2}{L}}$$

for comparison, the exact wave function evaluated at $x = \frac{L}{2}$:

$$\psi\left(x = \frac{L}{2}\right) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi(L/2)}{L}\right) = \sqrt{\frac{2}{L}} \quad \text{(close!)}$$

Q7 compare ψ_1(exact) and
φ (trial wave function)