Chemistry 410A

Exam 1 Solutions

- 1. (a) What is the frequency of the radiation at $\lambda = 1.0 \text{ m}$? Solution: $\nu = c/\lambda = 2.998 \cdot 10^8 \text{ m s}^{-1}/(1.0 \text{ m}) = 3.0 \cdot 10^8 \text{ s}^{-1}$.
 - (b) What is the energy in $E_{\rm h}$ of the n = 4 state of He⁺? Solution: $E_n = -Z^2 E_{\rm h}/(2n^2) = -2^2 E_{\rm h}/(2 \cdot 4^2) = \boxed{-\frac{1}{8} E_{\rm h}}.$
 - (c) The Bohr model of the atom successfully predicts which of the following:
 - i. The spectrum of the neutral helium atom.
 - ii. The wavefunction of the electron in the neutral hydrogen atom.
 - iii. The second ionization energy of the helium atom.

The Bohr model works only for one-electron atoms, and does *not* correctly predict the distribution of the electron.

- (d) A particle moves between two walls. The correspondence principle predicts that the system will behave more **classically** when we increase which of the following parameters:
 - i. The mass of the particle.
 - ii. The spacing between the walls.
 - iii. The de Broglie wavelength of the particle.
 - iv. The speed of the particle.

Increasing λ_{dB} relative to the domain *increases* quantum behavior.

2. For a continuous beam of free neutrinos (with $m = 1.0 \cdot 10^{-37}$ kg), sketch the probability density seen at a stationary detector as a function of time when $v_1 = 0.010c$. Label the numbers and units of the horizontal axis, but do not label the vertical axis.



Solution: (In the graph above, t is given in ns.) If the speed is well-defined, then wavefunction of the neutrinos will be $\sin(2\pi x/\lambda_{\rm dB})$, which is a sine wave with wavelength $\lambda_{\rm dB} = h/(mv)$. Using the speed to rewrite this as a function of time, we replace x with vt and obtain $\sin(2\pi v t/\lambda_{\rm dB}) = \sin(2\pi mv^2 t/h)$. This goes through one cycle of the wavefunction in time $\tau = h/(mv^2) = 7.4 \cdot 10^{-10}$ s for v_1 .

The detector sees only the probability density, which is proportional to the *square* of the wavefunction.

The whole experiment is speculative in the extreme. We don't actually have any idea what the neutrino mass is, although recent work indicates that neutrinos have masses less than 0.28 eV or $5 \cdot 10^{-37}$ kg. Neutrinos are also notoriously difficult to detect, let alone control to an extent were we can determine their speed. Still, they are intriguing because they are by far the lightest components of matter known to exist as independent particles, and λ_{dB} may be really *large*.

3. What is the eigenvalue when the \hat{p}^2 operator operates on the n = 2 state of a proton in a box of length 2.0 Å?

Solution: The quick way to answer this starts from the solution to the energy of the particle in a box, which is all kinetic energy, $mv^2/2 = p^2/(2m)$. (Because the wavefunction is an eigenfunction of the Hamiltonian, where $\hat{H} = -\hat{p}^2/(2m)$, $\psi(x)$ must also be an eigenfunction of \hat{p}^2 .)

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{p^2}{2m}$$

$$p^2 = 2mE_n = \frac{n^2 \pi^2 \hbar^2}{a^2}$$

$$= \frac{2^2 \pi^2 (1.055 \cdot 10^{-34} \,\mathrm{J\,s})^2}{(2.0 \cdot 10^{-10} \,\mathrm{m})^2} = \boxed{1.1 \cdot 10^{-47} \,\mathrm{kg}^2 \,\mathrm{m}^2 \,\mathrm{s}^{-2}}.$$

Operating on $\psi(x)$ with $\hat{p}^2 = -\hbar^2 \partial^2 / \partial x^2$ will yield the same result.

4. If the proton and the electron in the Bohr model of the hydrogen atom were replaced by uncharged particles with the same masses, what would be the ground state energy of this atom **in J**?

$$F_{\rm grav} = \frac{m_1 m_2 G}{r^2},$$

where $G = 6.67 \cdot 10^{-11} \,\mathrm{m}^3 \,\mathrm{kg}^{-1} \,\mathrm{s}^{-2}$. Solution: This expression for $F_{\rm grav}$ has the same dependence on distance as $F_{\rm Coulomb}$. The difference is that the constants $Ze^2/(4\pi\epsilon_0)$ have been replaced by m_1m_2G , where (since the masses are unchanged) $m_1m_2 = m_em_p$. We could follow the same steps used to obtain the Bohr energy expression, but since all we have done is change one set of constants for another, we can just take the result for the Bohr energy and change out those constants:

$$E_n = -\frac{Z^2 m_e e^4}{2(4\pi\epsilon_0)n^2\hbar^2}$$
 real atom, Eq. 1.20

$$E_n = -\frac{(m_e m_p G)^2 m_e}{2n^2\hbar^2}$$
 gravity atom

$$= -\frac{m_e^3 m_p^2 G^2}{2n^2\hbar^2}$$

For the ground state, we set n = 1:

$$E_1 = -\frac{(9.109 \cdot 10^{-31} \,\mathrm{kg})^3 (1.673 \cdot 10^{-27} \,\mathrm{kg})^2 (6.67 \cdot 10^{-11} \,\mathrm{m}^3 \,\mathrm{kg}^{-1} \,\mathrm{s}^{-2})^2}{2 (1.055 \cdot 10^{-34} \,\mathrm{J} \,\mathrm{s})^2} = \boxed{8.46 \cdot 10^{-97} \,\mathrm{J}.}$$

Comparing this to the ground state energy using the charged particles $(E_1 = 2.18 \cdot 10^{-18} \text{ J})$, you can see why we never worry about gravity when solving the quantum mechanics of atoms and molecules. Note: one topic of ongoing speculation among physicists is whether the gravitational force law stays the same at all distance scales. Although gravitational forces have been measured for individual neutrons, that was over distances of several microns – much larger than the distances separating subatomic particles in an atom. For a further exercise, try calculating the radius of the orbit of the particles in this gravity-atom.