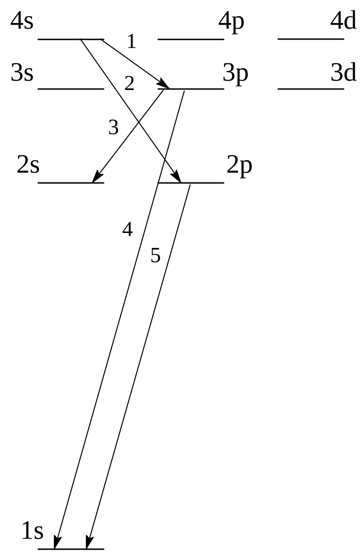
ChemE 2200 - Physical Chemistry II for Engineers
Solutions to Exercises for Calculation Session 1

1.(A) A convenient aid for predicting transitions is a Grotrian diagram,



Photons with 5 different energies will be detected. The most common errors were (1) predicting only 4 transitions because the 3p → 1s or 3p → 2s transition was missed and (2) predicting extra transitions because $E(2s) < E(2p)$ and $E(3s) < E(3p)$ which is not true for hydrogen atoms. $E(2s) = E(2p)$ and $E(3s) = E(3p)$ for hydrogen atoms.

(B) The key concept is $E_{photon} = E_{final} - E_{initial}$. For hydrogen atoms the energy levels are

$$E_n = -13.6\frac{1}{n^2}\text{ eV} = -109{,}677\frac{1}{n^2}\text{ cm}^{-1}$$

The photon energies are thus:

4s → 3p	0.66 eV
3p → 2s	1.89 eV
4s → 2p	2.55 eV
2p → 1s	10.2 eV
3p → 1s	12.1 eV

The most common error was to assume $\frac{1}{n^2} - \frac{1}{m^2} = \frac{1}{n^2 - m^2}$, which is not valid for any pair of integers n and m, such that $n \neq m$. (I would provide a proof, but there is too little space in the margin. So there, Fermat.)

(C) Ultimately, the electron of every hydrogen atom will relax to the 1s orbital. If the hydrogen atom's first transition is 4s → 2p, then its second transition must be 2p → 1s. Thus *every* atom that emits a photon at 2.55 eV will also emit a photon at 10.2 eV and thus these two peaks in the photon spectrum will have the same intensity. If a hydrogen atom instead begins with the transition 4s → 3p, the next transition may be either 3p → 2s or 3p → 1s. There is no guarantee that the latter two paths will have equal probability.

2.(A) Direct transition from H(2s) to H(1s) by photon emission is forbidden. We need to excite the H(2s) atoms to H atoms in p states; H(3p), or H(4p), etc. H atoms in p states may then relax to H(1s) directly by emitting a photon. The photon needed to excite from H(2s) to H(3p) has energy

$$E_{3p} - E_{2s} = -13.6\text{ eV}\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.89\text{ eV}$$

Thus we irradiate the sample with the photon source with energies 0.8 to 2.6 eV.

Here are some other considerations. What other transitions will this source excite? Check the energy for a transition from H(2s) to H(4p).

$$E_{4p} - E_{2s} = -13.6 \text{ eV}\left(\frac{1}{4^2} - \frac{1}{2^2}\right) = 2.55 \text{ eV}$$

So transitions from H(2s) to H(4p) will also induced. What about H(2s) to H(5p)?

$$E_{5p} - E_{2s} = -13.6 \text{ eV}\left(\frac{1}{5^2} - \frac{1}{2^2}\right) = 2.85 \text{ eV}$$

The energy difference between H(1s) and H(5p) is larger than the energy range of the photon source. So only the H(3p) and H(4p) states are produced. Note that the photons are not absorbed by the H(1s) atoms. The minimum energy required to excite a transition from a H(1s) state is a transition to H(2p).

$$E_{2p} - E_{1s} = -13.6 \text{ eV}\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 10.2 \text{ eV}$$

In summary, irradiate the sample with 0.8 to 2.6 eV photons. This will excite the H(2s) atoms to H(3p) and H(4p). In turn, these atoms will relax to H(1s), H(2s) and H(3s). The H(1s) will remain as such because they cannot absorb low energy photons. The H(2s) atoms will repeat the process. The H(3s) will relax to H(2p) by emitting a photon, then the H(2p) will relax to H(1s).

Note that you could assume the H(4p), H(3p), H(3s) and H(2p) will emit a photon immediately, before they could absorb another photon and then be excited to a yet-higher energy state.

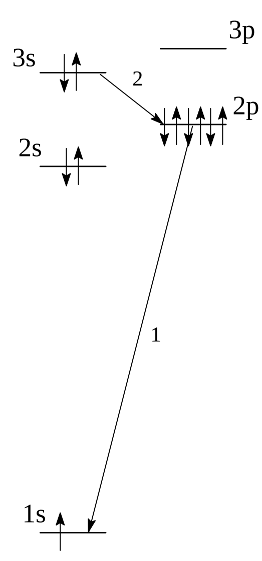
(B) If the process is working, the H atom gas will emit photons corresponding to the H(3p) $\rightarrow$ H(1s) transition (12.1 eV) and the H(4p) $\rightarrow$ H(1s) transition (12.8 eV). Detecting these two photons will be the primary evidence of success. Full credit was given for “look for 12.1 eV photons.”

There will also be photons from H(4p) $\rightarrow$ H(3s) transitions (0.66 eV), H(3s) $\rightarrow$ H(2p) transitions (1.89 eV), and H(2p) $\rightarrow$ H(1s) transitions (10.2 eV).

So, for the primary evidence, use the photon detector sensitive to photons in the range 10 to 20 eV. For the secondary evidence one can also use the 0.8 to 2.6 eV detector.

When this exercise appeared on an exam, 26 of the 77 sophomores sketched Grotrian diagrams. Five students put Schrödinger’s cat in the microwave oven.

3. The orbital occupancy of a Mg atom is $1s^2 2s^2 2p^6 3s^2$. The possible transitions are shown on the Grotrian diagram below.



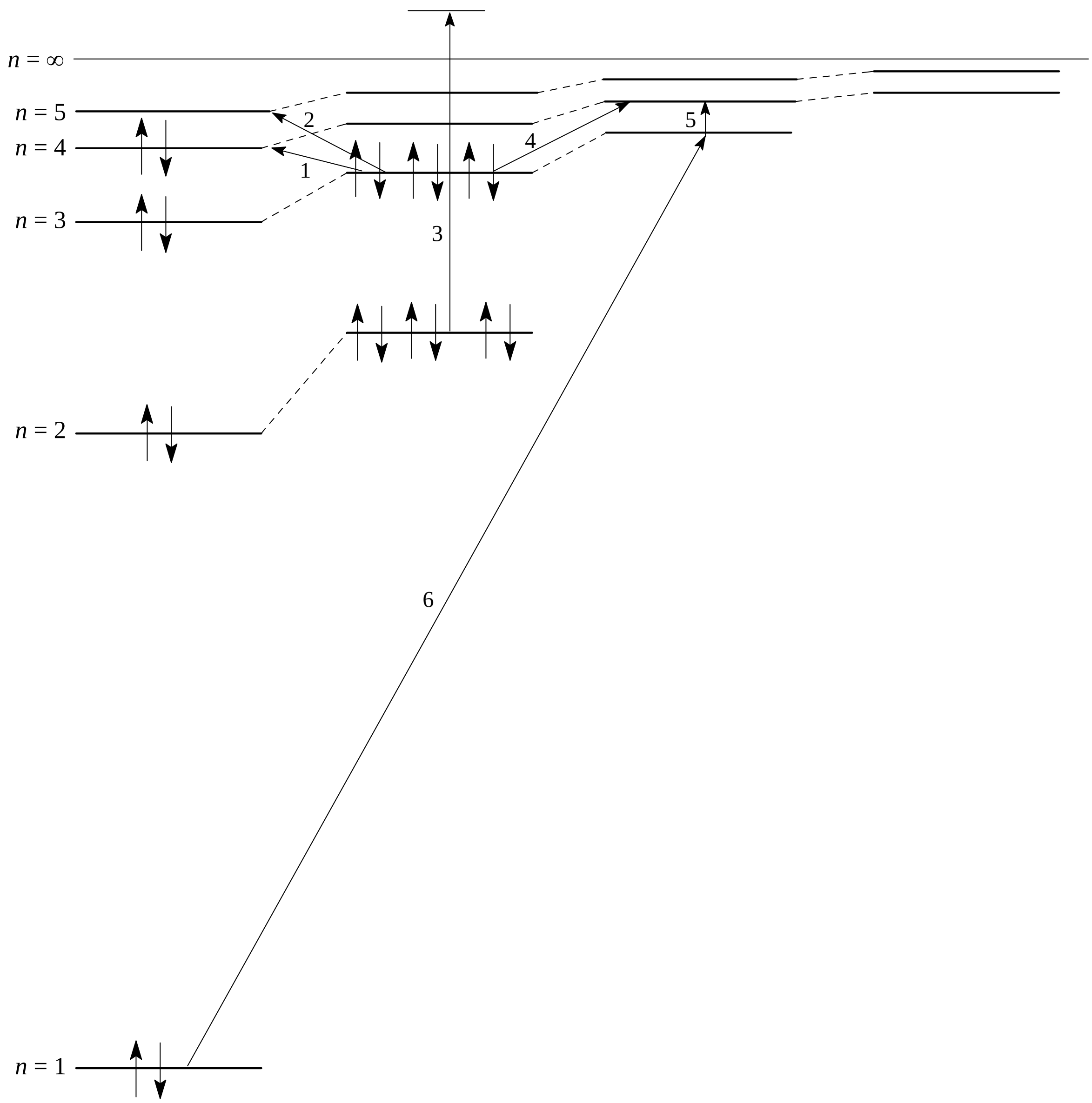
To start, a 1s electron is ejected. This allows a 2p electron to fall to the 1s vacancy (transition 1). This in turn allows a 3s electron to fall into the 2p vacancy (transition 2). Because 3s is the highest occupied level and because 2s → 1s transitions are forbidden, these are the only two photon energies emitted. The energies are as follows:

photon 1: $E_{photon} = E_{2p} - E_{1s} = -31\text{ eV} - (-153\text{ eV}) = 122\text{ eV}$

photon 2: $E_{photon} = E_{3s} - E_{2p} = -8.5\text{ eV} - (-31\text{ eV}) = 22.5\text{ eV}$

4. This exercise tests one's ability to allocate the 20 electrons of calcium and apply the selection rules for transitions. First, one must allocate the electrons as shown on the diagram below. This fills the energy levels through 4s ($n = 4$ and $\ell = 0$). The rules for allowed transitions are:

   1. The transition must originate at an energy level that has an electron.
   2. The transition must terminate at an energy level that has a vacancy.
   3. $\Delta\ell = \pm 1$.
   4. Δn = any integer.



transition	allowed?	reason
1	forbidden	No vacancy in the 4s level
2	allowed	$\Delta\ell = -1$
3	allowed	This is ionization. No restriction on $\Delta\ell$
4	allowed	$\Delta\ell = +1$
5	forbidden	$\Delta\ell = 0$ and the 3d level is empty
6	forbidden	$\Delta\ell = +2$

5.(A) ψ_1 not valid. Violates the Pauli Exclusion Principle. The 2 electrons in the $2p_x$ orbital have the same orbital quantum numbers ($n = 2$, $\ell = 1$, $m_\ell = 1$) and the same spin ($m_s = +½$)

ψ_2 valid.

ψ_3 valid.

ψ_4 valid.

ψ_5 not valid. A state function must be antisymmetric overall. A symmetric orbital term times a symmetric spin term yields a state function that is symmetric overall.

(B) Hund's rule says that the lowest energy state will have an antisymmetric orbital term. The only valid state function with an antisymmetric orbital term is ψ_3.

The Team Competition Champions for Calculation Session 1:

Team ‘A Team’

Eryk Nguyen, Emma Nam, and Anirudh Tenneti

Some of the questions, brief explanations, and the percent correct in 2023 are listed below.

Team Competition Questions:

Quantum mechanics predicts many surprising phenomena. Some phenomena seem incredulous because they are not observed in everyday settings (the macroscopic world).

Which of the following will not occur, even in quantum mechanics. That is, which of the following results are impossible and should motivate you to check your calculation.

1. Your prediction depends on the coordinate system you use. For example, in spherical coordinates you predict a probability of 0.48 and in Cartesian coordinates you predict a probability of 0.0001.

   IMPOSSIBLE (Correct Responses: 44%)

2. Your prediction is not exact. For example, you predict a particle's position is 3.423 ± 0.387 Å.

   POSSIBLE – Heisenberg Uncertainty Principle! (Correct Responses: 31%)

3. Your prediction is exact. For example, you predict a particle's energy is 10.47206509 eV, exactly.

   POSSIBLE – If the quantity measured is an eigenvalue, such as the energy of an electron in a hydrogen 1s orbital, the quantity has no uncertainty. (Correct Responses: 25%)

4. You measure a particle's property, then measure it again and obtain a different result. For example, you get different results when you measure the momentum of a free particle even though no force is acting on the free particle.

   POSSIBLE – Heisenberg Uncertainty Principle! (Correct Responses: 63%)

5. You measure a particle's property and get the same answer every time.

   POSSIBLE If the quantity measured is an eigen-value, such as the energy of an electron in a hydrogen 1s orbital, the quantity has no uncertainty. (Correct Responses: 69%)

6. The energy of a closed quantum mechanical system is not constant.

   IMPOSSIBLE – Energy is conserved, even in quantum mechanics. (Correct Responses: 56%)

7. The angular momentum of a closed quantum mechanical system is not constant.

   IMPOSSIBLE – Angular momentum is conserved, even in quantum mechanics. (Correct Responses: 56%)

8. The total electric charge of a closed quantum mechanical system is not constant.

   IMPOSSIBLE – Electric charge is conserved, even in quantum mechanics. (Correct Responses: 69%)

9. You predict that a particle's potential energy is greater than its total energy (which implies a negative kinetic energy, which implies a negative mass or imaginary velocity.)

   POSSIBLE – This is tunnelling! (Correct Responses: 56%)

10. Your prediction has units not normally expected for the quantity. For example, you predict that the particle's position is 3.2 joule.

    IMPOSSIBLE (Correct Responses: 88%)

11. The probabilities of mutually exclusive outcomes do not sum to 1. For example, you predict that after a given time there is a 0.60 probability that a certain particle remains in a box, and a 0.55 probability that it escaped the box.

    IMPOSSIBLE (Correct Responses: 69%)

12. For a one-dimensional system, you predict that a particle can move from one point to another, yet there is exactly zero probability the particle exists midway between the points.

    POSSIBLE – An electron in a hydrogen p orbital may exist in the +z lobe or in the -z lobe, but there is exactly zero probability the electron will ever be in the xy plane. The concept of a classical trajectory from one lobe to another is not valid in quantum mechanics. Think in terms of probabilities. (Correct Responses: 81%)