Chem 332 **Assignment #4** (***due Thursday 18 February, in class**)

***This assignment is *optional*. You lose no marks if it is not handed in. Happy "mini" study break.**

Q1. Give the **selection rules** for atomic spectroscopy. [1]

Q2. Ever wondered where **atomic orbital designations s, p, d, f** come from?

Spectroscopic studies of atomic sodium (ground-state electronic configuration [Ne]$3s^1$) gave series of emission lines for:

$ns^1 \rightarrow 3p^1$ transitions called the **sharp (s) series**
$np^1 \rightarrow 3s^1$ transitions called the **principal (p) series**
$nd^1 \rightarrow 3p^1$ transitions called the **diffuse (d) series**
$nf^1 \rightarrow 3d^1$ transitions called the **fundamental (f) series**

[4] The table below gives the energies in wavenumbers $(\tilde{E} = E / hc)$ of the first few excited states of sodium relative to the energy of the ground $3s^1$ electronic state. For these energy levels, calculate the frequencies (in wave numbers) for the allowed:

a) sharp transitions
b) principal transitions
c) diffuse transitions
d) fundamental transitions

(*Suggestion*: sketch the allowed transitions on energy-level diagrams)

configuration	**designation**	**J**	**energy/cm^{-1}**
[Ne]$3s^1$	^2S	1/2	0
[Ne]$3p^1$	^2P	1/2	16956.18
		3/2	16973.38
[Ne]$4s^1$	^2S	1/2	25739.86
[Ne]$3d^1$	^2D	5/2	29172.86
		3/2	29172.90
[Ne]$4p^1$	^2P	1/2	30266.88
		3/2	30272.51
[Ne]$5s^1$	^2S	1/2	33200.70
[Ne]$4d^1$	^2D	5/2	34548.75
		3/2	34548.79
[Ne]$4f^1$	^2F	5/2	34588.60
		7/2	34588.60

C. E. Moore, Atomic Energy Levels, *Natl. Bur. Std. Circ.* No. 467.

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Q3. The energies of sodium atoms given in **Q2** illustrate Hund's rules. Give two
[2] examples and explain why Hund's rules are obeyed.

Q4. How do the $^2D_{5/2}$ and $^2D_{3/2}$ states of [Ne]4d^1 sodium differ? To answer this question, sketch (to scale) of the vector addition of $\vec{L}$ and $\vec{S}$ to give the total
[4] angular momentum $\vec{J}$ for: **a)** the $^2D_{5/2}$ state **b)** the $^2D_{3/2}$ state

Hint: the angle θ between $\vec{L}$ and $\vec{S}$ is given by $|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 - 2|\vec{L}||\vec{S}|\cos\theta$

Q5. The energies of hydrogen and hydrogen-like atoms

$$E_n = -13.60 \text{ eV} \frac{Z^2}{n^2}$$

[1] increase as the principal quantum number n increases. But spectroscopic data for sodium (see **Q2**) show the sodium 4s energy is lower than the 3d energy. Also, the 5s energy level is below the 4d and 4f energies. How is this possible? Explain.

Q6. **a)** Derive the term symbols for the hydrogen atom in the 3d^1 state.

[4] **b)** Give the term symbol corresponding to the lowest hydrogen 3d^1 energy.

Q7. Show the atomic determinantal wave function $\psi = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$

a) is normalized (*Hint*: the 1s, α and β functions are normalized)

b) is antisymmetric

[3] **c)** factors into the product of a spatial function and a spin function.

Q8. Give a brief definition of a **spin orbital.** [1]

Q9. For a possible **bonus point**, explain why angular momentum decides the dates of **Ground Hog Day** (02 February) and **Halloween** (31 October).

[1?] *Hint*: orthodox Pagans can easily answer this question

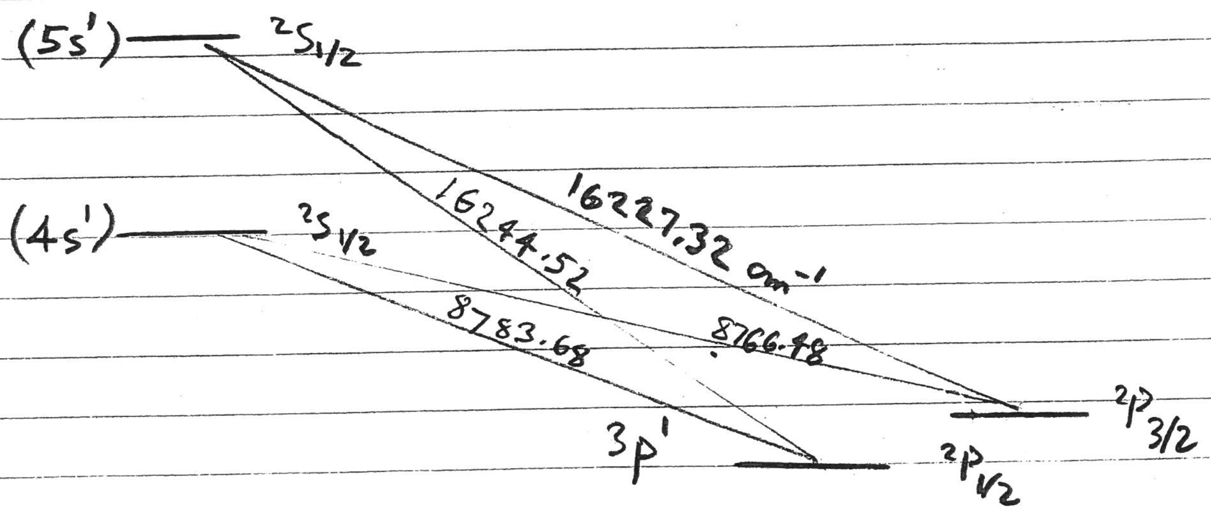
Chem 332 Assignment #4

Ⓠ1 main selection rules for atomic spectroscopy:

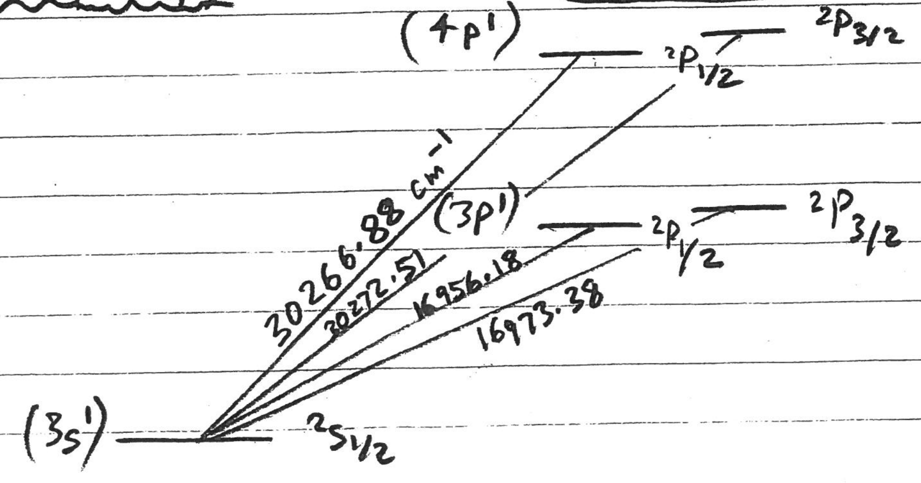
$\Delta L = \pm 1$ $\Delta J = 0, \pm 1$ $\Delta S = 0$

why? Absorption or emission of a photon usually has no effect on the electron spins ($\Delta S = 0$). A photon is a "boson" with spin 1 which gives $\Delta L = \pm 1$.

Ⓠ2 a) sharp (s) transitions $\boxed{ns^1 \rightarrow 3p^1}$

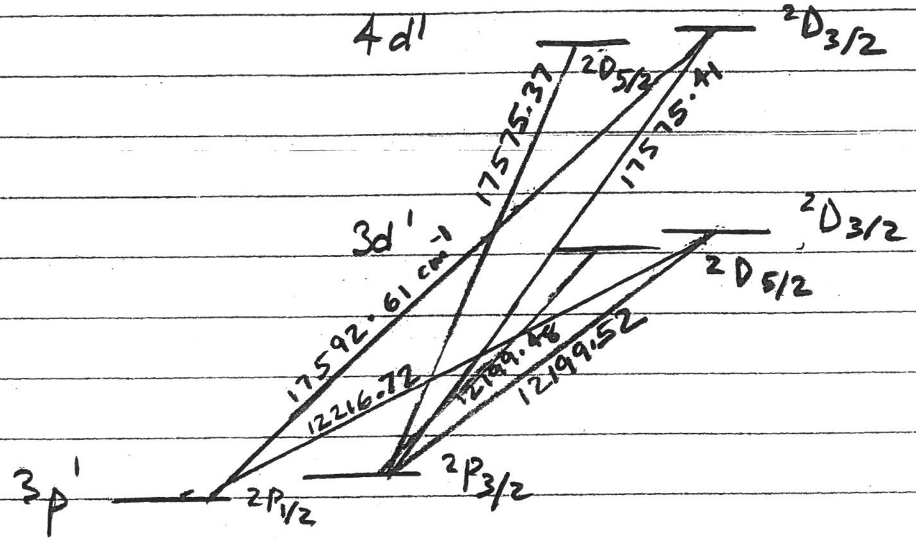


b) principal (p) transitions $\boxed{np^1 \rightarrow 3s^1}$

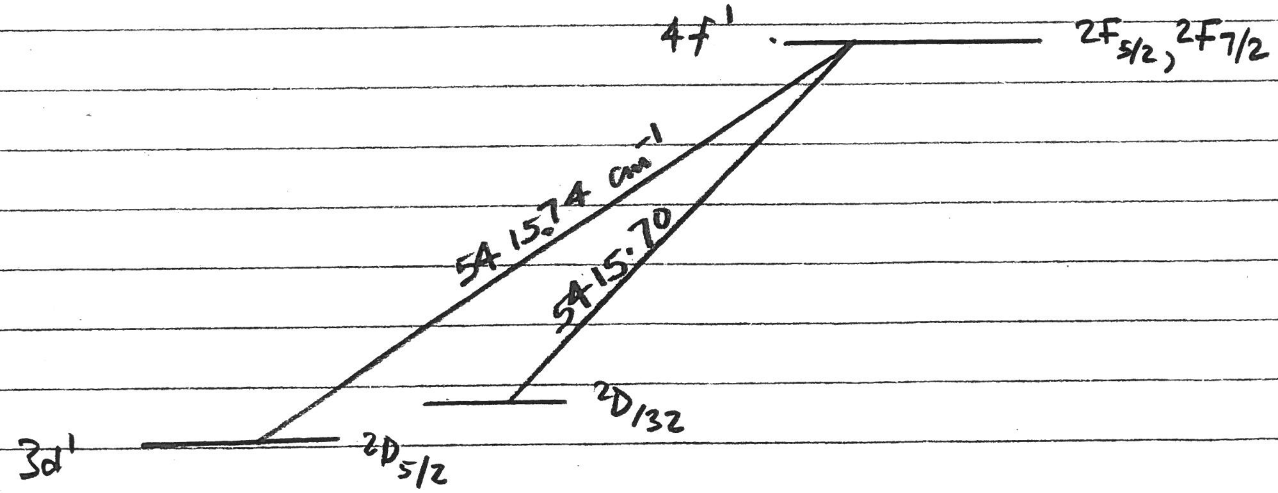


(Q2 cont.)

c) diffuse (d) transitions $nd^1 \rightarrow 3p^1$



d) fundamental (f) transitions $nf^1 \rightarrow 3d^1$



Q3 Do the energy levels of atomic sodium illustrate Hund's rules?

A) $^2P_{1/2}$ states are lower in energy than $^2P_{3/2}$ states
B) $^2D_{3/2}$ states are lower in energy than $^2D_{5/2}$ states

rule A: obeyed   rule B: not obeyed (Hund's rules are accurate only for ground configurations)

Q4 $^2D_{5/2}$ and $^2D_{3/2}$ states have

identical orbital angular momentum ($L = 2$) and identical spin angular momentum ($S = 1/2$) but combine ("couple") to give different total angular momentum

a) $^2D_{5/2}$ state $L = 2$ $S = \frac{1}{2}$ $J = 5/2$

$$|\vec{L}| = \sqrt{L(L+1)}\,\hbar \qquad |\vec{S}| = \sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)}\,\hbar \qquad |\vec{J}| = \sqrt{\tfrac{5}{2}\left(1+\tfrac{5}{2}\right)}\,\hbar$$

$$= \sqrt{6}\,\hbar \qquad = \sqrt{\tfrac{3}{4}}\,\hbar \qquad = \sqrt{\tfrac{35}{4}}\,\hbar$$

$$= 2.45\ldots\,\hbar \qquad = 0.866\ldots\,\hbar \qquad = 2.95\ldots\,\hbar$$

$$\cos\theta = \frac{-|\vec{J}|^2 + |\vec{L}|^2 + |\vec{S}|^2}{2|\vec{L}||\vec{S}|} = \frac{-\frac{35}{4} + 6 + \frac{3}{4}}{2\sqrt{6}\sqrt{\frac{3}{4}}} = -0.4714\ldots$$

$\theta = 118.1°$

b) $^2D_{3/2}$ state $\quad L = 2 \quad S = 1/2 \quad J = 3/2$

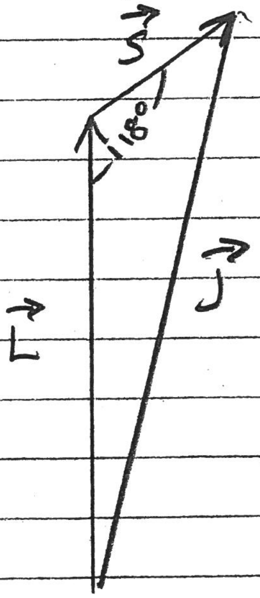
$$|\vec{L}| = \sqrt{L(L+1)}\,\hbar = \sqrt{6}\,\hbar = 2.45\ldots\,\hbar$$

$$\vec{S} = \sqrt{S(S+1)}\,\hbar = \sqrt{3/4}\,\hbar = 0.866\ldots\,\hbar$$

$$\vec{J} = \sqrt{J(J+1)}\,\hbar = \sqrt{\tfrac{3}{2}\left(\tfrac{5}{2}\right)}\,\hbar = 1.94\ldots\,\hbar$$

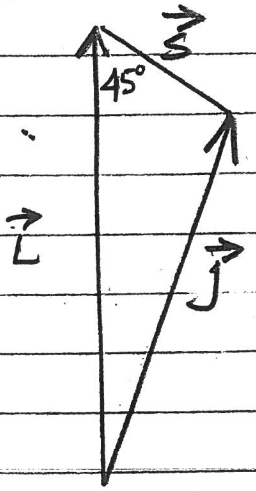
$$\cos\theta = \frac{-\left(\frac{3}{2}\right)\left(\frac{5}{2}\right) + 6 + \frac{3}{4}}{2\sqrt{6}\sqrt{3/4}} = 0.7071\ldots$$

$$\theta = 45^\circ$$



$^2D_{5/2}$

$\vec{L}$ and $\vec{S}$ partially combine to give $J = 5/2$



$^2D_{3/2}$

$\vec{L}$ and $\vec{S}$ partially cancel to give less total angular momentum, $J = 3/2$

Q5 For sodium, the $4s^1$ energy drops below the $3d^1$ energy

and the $5s^1$ energy drops below the $4d^1$ energy

But for hydrogen atoms, (only 1 electron) $4s^1$ energy > $3d^1$ energy
$5s^1$ energy > $4d^1$ energy
because energies are decided entirely by the principle quantum number n of the ns, nd levels (no shielding for H atoms – only one electron)

Sodium atoms are multi-electron atoms. The $4s^1$ electron is more compact and experiences less shielding from the nucleus than $3d^1$ electrons, lowering its energy

Ditto for the $5s^1$ and $4d^1$ levels,

Q6 $3d^1$ state of atomic hydrogen $\begin{pmatrix} l=2 & n=3 \\ m = -2, -1, 0, 1, 2 \end{pmatrix}$

m = −2	−1	0	1	2	M	M_s	J_s
↑					−2	1/2	−1 1/2
	↑				−1	1/2	−1/2
		↑			0	1/2	1/2
			↑		1	1/2	1 1/2
				↑	2	1/2	2 1/2
↓					−2	−1/2	−2 1/2
	↓				−1	−1/2	−1 1/2
		↓			0	−1/2	−1/2
			↓		1	−1/2	1/2
				↓	2	−1/2	1 1/2

(Q6 cont.)

notice: 2 sets of $M = -2, -1, 0, 1, 2$ values $(L=2)$

$\Rightarrow$ two D states

$M_S = \pm 1/2 \Rightarrow S = 1/2$ doublets $(2S+1=2)$

$\vec{L}$ and $\vec{S}$ can add to give a larger $\vec{J}$ (total angular momentum)

$$J = L + S = 2 + 1/2 = 5/2$$

or subtract to give a smaller J

$$J = L - S = 2 - 1/2 = 3/2$$

gives term symbols ${}^2D_{5/2}$ and ${}^2D_{3/2}$

b) For atoms with the same L and S values (2 and 1/2 here) with a subshell less than half filled (applies here with only one electron in the $3d^1$ state, a subshell that can hold up to 10 electrons), Hund's rules say the ${}^2D_{3/2}$ energy is lower (smallest J value if L, S are identical) n electron 1 electron 2

Q7 a) $$\psi = \frac{1s(1)\alpha(1)\,1s(2)\beta(2) - 1s(2)\alpha(2)\,1s(1)\beta(1)}{\sqrt{2}}$$

ψ is real, so $\psi^* = \psi$

Is ψ normalized?

$$\int \psi^* \psi \, d\tau = \int (\psi^*)^2 d\tau$$

$$= \int \left(\frac{1s(1)\alpha(1)\,1s(2)\beta(2) - 1s(2)\alpha(2)\,1s(1)\beta(1)}{\sqrt{2}} \right)^2 d\tau$$

($\alpha(1), \beta(1)$ and $\alpha(2), \beta(2)$ are orthonormal)

$$= \frac{1}{2} \int \left[[1s(1)\alpha(1)\,1s(2)\beta(2)]^2 - 2(1s(1)\alpha(1)\,1s(2)\beta(2)\,1s(2)\alpha(2)\,1s(1)\beta(1)) + [1s(2)\alpha(2)\,1s(1)\beta(1)]^2 \right] d\tau$$

$$= \frac{1}{2} \int \cancelto{1}{1s^2(1)\, d\tau_1} \int \cancelto{1}{1s^2(2)\, d\tau_1} \int \cancelto{1}{\alpha^2(1)\, d\sigma_1} \int \cancelto{1}{\beta^2(2)\, d\sigma_2}$$

$$- 2 \int \cancelto{1}{1s^2(1)\, d\tau_1} \int \cancelto{1}{1s^2(2)\, d\tau_1} \int \cancelto{0}{\alpha(1)\beta(1)\, d\sigma_1} \int \cancelto{0}{\alpha(2)\beta(2)\, d\sigma_2}$$

$$+ \frac{1}{2} \int \cancelto{1}{1s^2(1)\, d\tau_1} \int \cancelto{1}{1s^2(2)\, d\tau_2} \int \cancelto{1}{\alpha^2(2)\, d\sigma_2} \int \cancelto{1}{\beta^2(2)\, d\sigma_2}$$

$$= \frac{1}{2}(1) - 2(0) + \frac{1}{2}(1)$$

$$= 1$$

$\therefore \psi^*$ is normalized

(Q7 cont.)

b) $$\psi(1,2) = \frac{1s\,\alpha(1)\ 1s\,\beta(2) - 1s\,\alpha(2)\ 1s\,\beta(1)}{\sqrt{2}}$$

interchanging electrons 1 and 2 gives

$$\psi(2,1) = \frac{1s\,\alpha(2)\ 1s\,\beta(1) - 1s\,\alpha(1)\ 1s\,\beta(2)}{\sqrt{2}}$$

$$= -\frac{1s\,\alpha(1)\ 1s\,\beta(2) - 1s\,\alpha(2)\ 1s\,\beta(1)}{\sqrt{2}}$$

$\psi(2,1) = -\psi(1,2)$ ("symmetric" would mean $\psi(1,2) = \psi(2,1)$ (not here))

$\Rightarrow \psi$ is "antisymmetric"

c) $$\psi(1,2) = \frac{1s(1)\,\alpha(1)\ 1s(2)\,\beta(2) - 1s(2)\,\alpha(2)\ 1s(1)\,\beta(1)}{\sqrt{2}}$$

$$= \frac{[1s(1)\,1s(2)]\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}{\sqrt{2}}$$

the product of spatial $\frac{1s(1)\,1s(2)}{\sqrt{2}}$

and spin $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ factors

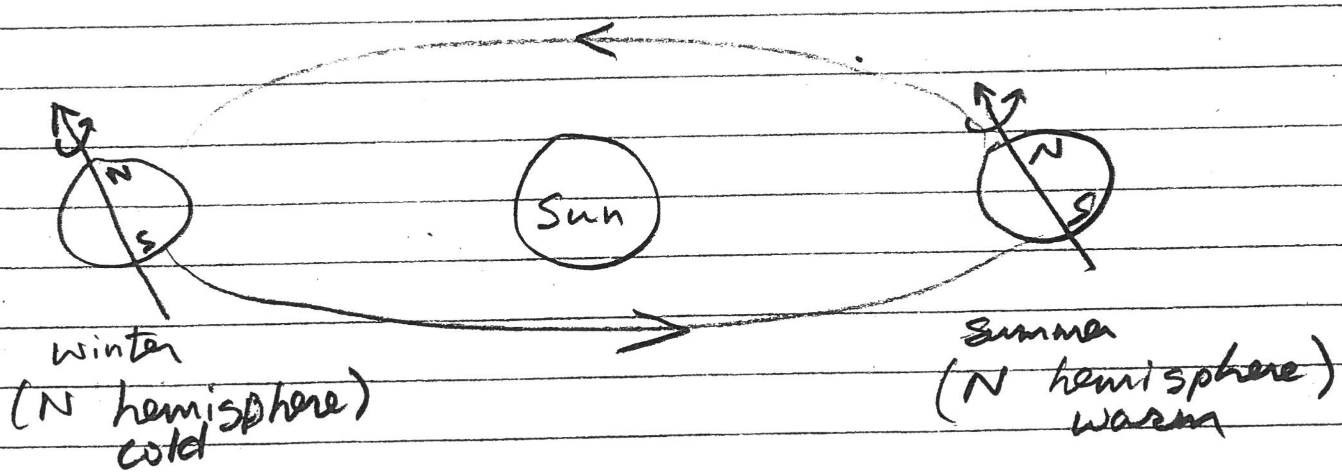
important consequence: a spatial wave of function of incorrect symmetry (ie., symmetric) can be "corrected" by an antisymmetric spin function, and vice versa

Q8 a spin orbital is the product of a spatial wave function of the hydrogen atom (e.g. $\overset{(1s)}{\psi_{100}}$ for the ground state) multiplied by a spin wave function $(\overset{\uparrow}{\alpha}$ or $\overset{\downarrow}{\beta})$

from the Exclusion Principle, only one electron can occupy a given spin orbital

(e.g. $\underset{(1s\alpha)}{\psi_{100}\alpha}$, $\underset{1s\beta}{\psi_{100}\beta}$, ...)

Q9 conservation of angular momentum gives us the seasons: spring, summer, fall, winter



Ground Hog Day ≃ half way between the winter solstice (≃ Dec 21) and the spring equinox (≃ March 21)

Halloween ≃ half way between the fall equinox (≃ Sept 21) and the winter solstice (≃ Dec 21)