Final Solutions

1. *To figure out electronic configurations of multi-electron atoms we have to take inter-electron Coulomb repulsion into account. For relatively small atoms, we can ignore spin-orbit interactions (in comparison to Coulomb repulsion), and build electronic configurations using LS coupling. Namely, we add individual* l *to form a total* L*, and individual* s *to form total* S*. We then refer to the configuration as* ${}^{2S+1}L$*, such as* ${}^{1}P$*,* ${}^{3}D$*, etc. With the central potential alone electronic configurations with the orbitals are degenerate. However, inter-electron Coulomb repulsion removes the degeneracy. The empirical "Hund's rule " says that configuration with larger* S *are lower, and among those with the same* S*, states with larger* L *are lower. Calculate the difference in energies for three different configurations for the case of carbon* $1s^2 2s^2 2p^2$*, and show that Hund's rule is correct. For this purpose, you can ignore the completely filled* $1s$ *and* $2s$ *orbitals, and discuss only the remaining two electrons in the* $2p$ *orbital (of course anti-symmetrized) and the Coulomb repulsion between them*

A good place to begin is to recognize which electronic configurations are allowed by anti-symmetry of the wavefunction. We are adding two spin 1/2 particles which can give us an antisymmetric $S = 0$ or a symmetric $S = 1$. Adding the two $l = 1$ states can give either $L = 0$ or $L = 2$ which are symmetric[1] or an antisymmetric $L = 1$, requiring the total wave function be antisymmetric we are restricted to

$$ {}^{1}S \qquad {}^{3}P \qquad {}^{1}D $$

in the notation described above. Hund's rule then predicts

$$E_{^3P} < E_{^1D} < E_{^1S}.$$

The configurations $|L, m_L\rangle \times |\text{spin}\rangle$ above may be written in terms of the individual angular momentum eigenstates $|l_1, m_1\rangle \times |l_2, m_2\rangle \equiv |m_1, m_2\rangle$ as follows:

- For the ${}^{1}D$ states:

$$\begin{aligned}
|2, +2\rangle &= |+1, +1\rangle \\
|2, +1\rangle &= \frac{1}{\sqrt{2}} \left(|+1, 0\rangle + |0, +1\rangle\right) \\
|2, 0\rangle &= \frac{1}{\sqrt{6}} \left(|+1, -1\rangle + |-1, +1\rangle + 2|0, 0\rangle\right) \\
|2, -1\rangle &= \frac{1}{\sqrt{2}} \left(|-1, 0\rangle + |0, -1\rangle\right) \\
|2, -2\rangle &= |-1, -1\rangle
\end{aligned} \tag{1}$$

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[1] Note that we are referring to symmetry under exchange of particles. The general rule is that the highest L is symmetric, and then alternate.

times an antisymmetric spin state.

- For the ^3P states

$$\begin{aligned}|1,+1\rangle &= \frac{1}{\sqrt{2}}\left(|+1,0\rangle - |0,+1\rangle\right) \\ |1,0\rangle &= \frac{1}{\sqrt{2}}\left(|+1,-1\rangle - |-1,+1\rangle\right) \\ |2,-1\rangle &= \frac{1}{\sqrt{2}}\left(|-1,0\rangle - |0,-1\rangle\right) \qquad (2)\end{aligned}$$

  times a symmetric spin state.

- For the ^1S state

$$|0,0\rangle = \frac{1}{\sqrt{3}}\left(|+1,-1\rangle + |-1,+1\rangle - |0,0\rangle\right) \qquad (3)$$

  times an antisymmetric spin state.

To demonstrate Hund's rule we will ignore the electrons in the closed shell as instructed and only look at the two outer electrons in the $2p$ orbital moving in some central potential $W(r)$ that will include the screening of the nuclear charge by inner orbitals. Just as we did with the helium atom we will calculate the energy treating the Coulomb repulsion as a perturbation,

$$\begin{aligned}H &= H_0 + V \\ H_0 &= \sum_{i=1,2}\left(\frac{p_i^2}{2m} + W(r_i)\right) \\ V &= \frac{e^2}{r_{12}}.\end{aligned}$$

Ignoring the Coulomb repulsion, all of the configurations above are degenerate[2]. To first order in perturbation theory, the shift in energy is the usual $\langle\psi|V|\psi\rangle$, where $|\psi\rangle$ is any of the allowed configurations above. The next question is: when calculating shift in energy for ^1D, for example, which of the configurations in Eq. (1) should we take? Since $\frac{1}{r_{12}}$ is rotationally invariant ($\hat{L}$ commutes with H) we are guaranteed to get the same result for any m_L, once we chose L. It is of course most convenient to choose $|2,+2\rangle$ in the ^1D case because it consists of only one

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[2] This is actually an assumption that $W(r)$ falls like r^{-1} where the ^2p orbital is peaked. Namely, we assume the ^1s and ^2s are closer to the nucleus than ^2p, and the screening is already 'exhausted' at the typical distance of the ^2p orbital. This assumption is needed to prevent an L-depending energy such as in question 1 part b) of the midterm. I hope you agree it is a reasonable assumption.

term, but we will have to deal with more than one when calculating for the other configurations. In the notebook attached we do the calculation for all possible values of m_L to illustrate this degeneracy.

As an example lets look at $|L = 1, m_L = +1\rangle$. Plugging the appropriate configuration in Eq. (2) we get

$$\begin{aligned} &\Delta E_{^3p} = \\ &= \frac{1}{2}\left[\langle +1,0|V|+1,0\rangle - \langle +1,0|V|0,+1\rangle - \langle 0,+1|V|+1,0\rangle + \langle 0,+1|V|0,+1\rangle\right] \\ &= \langle +1,0|V|+1,0\rangle - \langle +1,0|V|0,+1\rangle. \qquad (4) \end{aligned}$$

So in general we want to calculate matrix elements of the form $\langle m_1, m_2|\frac{e^2}{r_{12}}|m_3, m_4\rangle$. We will use the standard expansion of the coulomb repulsion

$$\frac{1}{r_{12}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\Omega_2) Y_{lm}(\Omega_1). \qquad (5)$$

Since Eq. (5) has a spherical harmonic for each electron and the bra and ket will have one more each, we will have to perform a 'triple-Y_{lm}' integral for each electron (we've done this before but in previous cases one of them was Y_{00}). Luckily, such a triple-Y integral is given in terms of Clebsch-Gordan (CG) coefficients (Eq. 3.7.73 in the first Sakurai)

$$\begin{aligned} &\int d\Omega Y_{lm}^*(\Omega) Y l_1 m_1(\Omega) Y_{l_2 m_2}(\Omega) \\ &= \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} \langle l_1, 0; l_2, 0|l, 0\rangle \langle l_1, m_1; l_2, m_2|l, m\rangle \qquad (6) \end{aligned}$$

where $\langle l_1, m_1; l_2, m_2|l, m\rangle$ is a CG coefficient that is non-zero only when $l_1 + l_2 \geq l \geq |l_1 - l_2|$ and $m = m_1 + m_2$. Note that for $l_1 = l_2 = 1$ the only values l takes in Eq. (6) are $l = 0$ or 2 because of the first CG coefficient (this coefficient vanishes for l=1 because of parity). We will assume the radial wave function that solves $W(r)$ is some $R(r)$ such that

$$\psi(\vec{r}_1, \vec{r}_2) = R(r_1)R(r_2) \times [\text{angular part}] \times [\text{spin part}] \qquad (7)$$

Putting it all together, changing the names of some indices, gives a relatively simple expression for the matrix element (defined as `me[ ]` in the attached Mathematica notebook)

$$\begin{aligned} &\langle m_1, m_2|\frac{e^2}{r_{12}}|m_3, m_4\rangle = \\ &\sum_{l=0,2} F_l \sum_{m=-l}^{l} \langle 1,0;1,0|1,0\rangle^2 \langle 1, m_1; l, m|1, m_3\rangle \langle 1, m_2; l, m|1, m_4\rangle \qquad (8) \end{aligned}$$

with

$$F_l = e^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 R^*(r_1) R^*(r_2) \frac{r_<^l}{r_>^{l+1}} R(r_1) R(r_2) \tag{9}$$

If you haven't done so before, now is the time to take a look at the Mathematica notebook. Writing the energy shift in terms of matrix elements such as in Eq. (4) and working out the CG coefficient carnival shows us the following

$$\begin{aligned} \Delta E_{^3P} &= F_0 - \frac{1}{5}F_2 \\ \Delta E_{^1D} &= F_0 + \frac{1}{25}F_2 \\ \Delta E_{^1S} &= F_0 + \frac{2}{5}F_2. \end{aligned} \tag{10}$$

Note that we got the same results for all m_L in a certain multiplet. Just by looking at the definition of F_l we see that it is positive. Eq. (10) is therefore a confirmation of Hund's rule. Note that we have not yet performed the radial integral. This shows that Hund's rule works regardless of the amount of screening by inner orbitals (so long as the screening satisfies the assumption we made in the footnote above). The next step is to take an explicit form for W(r)

$$W(r) = \frac{e^2 Z_{eff}}{r},$$

where Z_{eff} will be expected to be somewhere between 2 and 6 (2 for maximal screening and 6 for no screening. I'd guess closer to 2). This form for $W(r)$ is framiliar— the radial part of the wavefunction will be the usual hydrogen atom $R_{2p}(r)$ with $Z \to Z_{eff}$. Doing the radial integrals gives the results shown in the notebook. The energy differences are of order 1 eV, much smaller than the carbon binding energy which of order a few hundred eV.

2. *Consider the decay of the* $2p$ *state of hydrogen atom to the* $1s$ *state. Calculate the amplitude of the decay for* $m = +1$ *state using plane waves for photons, and explain the* θ *dependence of the amplitude for each helicity* ± 1 *of the final-state photon in terms of the angular momentum conservation. Show that the rate is the same as the decay rate of the* $m = 0$ *state.*

The only differences from the calculation in the lecture note "Quantum Field Theory III (Radiation Field)" are: the matrix elements $\langle 1s|\vec{D}|2p, m = \pm 1\rangle$ and the polarization vectors $\vec{\epsilon}_\lambda(\vec{q})^*$. (The complex conjugation is very important for helicity eigenstates.) The matrix elements are

$$\langle 1s|\vec{D}|2p, m = 1\rangle = e\int_0^\infty r^2 dr d\Omega \frac{1}{a^3} 2e^{-r/a} Y_0^{0*} \frac{\sqrt{6}}{12}\frac{r}{a} e^{-r/2a} Y_1^1 \vec{x}. \tag{11}$$

Because $Y_1^1 = -\sqrt{3}8\pi \cos\theta e^{i\phi}$, only x and y components of the dipole operator survive integration over ϕ. The result of the integration is

$$\langle 1s|\vec{D}|2p, m=1\rangle = -e\frac{128}{243}a(1, i, 0). \tag{12}$$

On the other hand, the polarization vectors for helicity ±1 states are (Eqs. (16,17,18) in the lecture note):

$$\epsilon_\pm(\vec{p}) = \frac{1}{\sqrt{2}}(\pm\cos\theta\cos\phi - i\sin\phi, \pm\cos\theta\sin\phi + i\cos\phi, \mp\sin\theta). \tag{13}$$

Therefore the transition matrix element Eq. (56) is

$$\begin{aligned}
\langle f|V|i\rangle &= \frac{i}{\hbar}|\vec{q}|\sqrt{\frac{2\pi\hbar c^2}{L^3}}\frac{1}{\sqrt{\omega_q}}\vec{\epsilon}^*_\lambda(\vec{q})\cdot\langle 1s|\vec{D}|2p, m=1\rangle \\
&= \frac{i}{\hbar}|\vec{q}|\sqrt{\frac{2\pi\hbar c^2}{L^3}}\frac{1}{\sqrt{\omega_q}}(-e)\frac{128}{243}a \\
&\quad (1, i, 0)\cdot\frac{1}{\sqrt{2}}(\pm\cos\theta\cos\phi + i\sin\phi, \pm\cos\theta\sin\phi - i\cos\phi, \mp\sin\theta) \\
&= \frac{i}{\hbar}|\vec{q}|\sqrt{\frac{2\pi\hbar c^2}{L^3}}\frac{1}{\sqrt{\omega_q}}(-e)\frac{1}{\sqrt{2}}\frac{128}{243}a(1\pm\cos\theta)e^{i\phi}.
\end{aligned} \tag{14}$$

The θ dependence has a simple interpretation in terms of angular momentum conservation. The initial state has the angular momentum $J_z = +1$. When a positive helicity photon is emitted along the negative z-axis, it carries away the angular momentum $J_z = -1$, and hence the final state must have $J_z = +2$. However, our final state is $1s$ and hence $J_z = 0$. Such a transition must be forbidden. Indeed, $(1+\cos\theta)$ factor does that precisely. Only the other hand, if the positive helicity photon is emitted along the positive z-axis, the angular momentum conservation is satisfied. Since unit angular momentum should give an amplitude linear in $\cos\theta$ (in general higher j gives j-th order polynomials), $(1+\cos\theta)$ is the only possible θ dependence. The argument for a negative helicity photon is similar.

The rate is calculated in the same way as in Eq. (60),

$$\begin{aligned}
W_i &= \int\frac{d\Omega_q}{(2\pi\hbar)^3}|\vec{q}|^2\frac{(2\pi)^2|\vec{q}|}{\hbar}\sum_\pm\left|(-e)\frac{1}{\sqrt{2}}\frac{128}{243}a(1\pm\cos\theta)e^{i\phi}\right|^2 \\
&= \int\frac{d\Omega_q}{2\pi\hbar^4}|\vec{q}|^3\sum_\pm\left(e\frac{1}{\sqrt{2}}\frac{128}{243}a\right)^2(1\pm 2\cos\theta+\cos^2\theta) \\
&= \int\frac{d\Omega_q}{2\pi\hbar^4}|\vec{q}|^3\left(e\frac{1}{\sqrt{2}}\frac{128}{243}a\right)^2 2(1+\cos^2\theta)
\end{aligned}$$

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\begin{aligned}
&= \frac{8}{3}\left(\frac{128}{243}\right)^2 e^2 \frac{q^3 a^2}{\hbar^4} \\
&= \frac{2}{3}\left(\frac{256}{243}\right)^2 e^2 \frac{q^3 a^2}{\hbar^4}. \qquad (15)
\end{aligned}
$$

Note that you need to sum over helicities of the photon to obtain the total decay rate of the $2p$ state. This result agrees completely with the decay orate of the $|2p, m=0\rangle$ state calculated in the lecture note, confirming the rotational invariance of the result.

3. *How can the* $2s$ *state decay to the* $1s$ *state? You do not need to calculate the rate, but sketch how the calculation can be done, and also give an estimate of the rate.*

In multipole expansion, we saw that a photon carries angular momentum of *at least* one. On the other hand, the initial and final state here both have zero angular momentum. Therefore, the $2s$ state *cannot* decay to the $1s$ state by emitting a single photon. When you were told that Lyman series of hydrogen spectrum shows transitions between states with principal angular momentum n and 1, you were cheated; $n=1$ case shows only transitions between $2p$ and $1s$, but *not* $2s$! Then how does the $2s$ state decay to the ground state? It has to emit *two* photons. Note that an emission of two photons at the same time does not give you a discrete spectrum. Only the sum of two photon energies is constrained. The dominant contribution is the emission of two photons both in the E1 multipole (electric dipoles) where the angular momenta of both photons cancel and hence they are in the $J=0$ configuration. Angular momentum consideration suggests the combination $|k10, k10\rangle + 2|k11, k1-1\rangle$.

Then the next question is how can two photons be emitted. There are two possibilities. One is to use the term

$$V = \left(\frac{e}{c}\right)^2 \vec{A}(\vec{x})^2 \qquad (16)$$

in the Hamiltonian. However, using the expression for the electric dipole photon Eq. (86) in the lecture note, the matrix is $\langle 1s|2s\rangle$ which vanishes identically. Then we have to go to higher order in kr for the electric dipole mode function $\vec{u}^E_{k10}$. Another possibility is to use the operator we've been using

$$V = -\frac{e}{c}\vec{p}\cdot\vec{A}(\vec{x}) \qquad (17)$$

twice. The transition element is then

$$\langle 1s + \text{two photons}|V\frac{1}{E_{2s}-H_0}V|2s\rangle = \sum_i \langle 1s + \text{two photons}|V|i\rangle \frac{1}{E_{2s}-E_i}\langle i|V|2s\rangle. \qquad (18)$$

The perturbation Hamiltonian V on the left creates the intermediate states, $|2p + \text{photon}\rangle$ (or any other $|np\rangle$ state), while that on the right creates another photon making transition to the $1s$ state. You then have to sum over all intermediate states.

Order of magnitude of the process can be easily be estimated by neglecting all numerical factors but by keeping dependences on the physical constants. We have seen that dipole transition matrix elements $\langle f|V|i\rangle$ go as $\sim ea_0 E_\gamma^{1/2} L^{-3/2}$. Then the transition element Eq. (18) goes as

$$\sum_i \langle 1s + \text{two photons}|V|i\rangle \frac{1}{E_{2s} - E_i} \langle i|V|2s\rangle \sim (ea_0 E_\gamma^{1/2} L^{-3/2})^2 \frac{1}{e^2/a_0} = a_0^3 E_\gamma L^{-3}. \tag{19}$$

Doing a similar analysis for the contribution from the term Eq. (16) shows that it is suppressed by at least α^2 because of the higher order in the multipole expansion. The rate goes as square of this: $a_0^6 E_\gamma^2 L^{-6}$. The phase space integral summing over two final state photons goes as $(L^3 q^3/\hbar^3)^2 \sim L^6 E_\gamma^6/(\hbar c)^6$. Here I made an approximation that two photon energies are comparable. This is indeed the case because the phase space $E_1^3 E_2^3$, subject to the constraint that $E_1 + E_2$ is fixed, is maximized when $E_1 \sim E_2$. Together with the delta function in energy and $1/\hbar$ in Fermi's golden rule, the estimate of the decay rate is $a_0^6 E_\gamma^7/\hbar^7 c^6 \simeq \alpha^8 mc^2/\hbar$. On the other hand, the dipole transition rate for $2p \to 1s$ is $\alpha^5 mc^2/\hbar$ up to numerical factors. Therefore, the decay rate of $2s \to 1s$ is roughly $\alpha^3 \simeq 4 \times 10^{-7}$ smaller.

A detailed calculation shows that the decay rate is very small: 8.229 sec^{-1}, even another order of magnitude smaller than the above rough estimate due to numerical factors. This is smaller than the dipole transition from $2p$ to $1s$ by eight orders of magnitude! The $2s$ state is hence said to be *metastable*.

You may think that the $2s$ state decays into $2p$ state first, which is lower than the $2s$ state because of the Lamb shift, and then decays into $1s$ state, rather than going through quantum intermediate states as in Eq. (18) or emitting two photons directly from the operator Eq. (16). Recalling that the decay rate due to electric dipole transition is proportional to the energy of the photon to the cube power, and knowing that the decay rate we calculated for $2p \to 1s$ was $6.27 \times 10^8 \text{sec}^{-1}$, we can estimate the order of magnitude of the decay rate of $2s$ to $2p$ due to the Lamb shift. The level splitting is about 1 GHz in frequency. The energy of the photon then is $h\nu \simeq 4.1 \times 10^{-6}$ eV. On the other hand, the energy of the photon in the $2p \to 1s$ decay is $13.6 \times (1 - 1/4)$ eV. Therefore the $2s \to 2p$ decay gives the energy of the photon 4.1×10^{-7} time smaller than $2p \to 1s$, and hence the decay rate is suppressed by $(4.1 \times 10^{-7})^3 = 6.7 \times 10^{-20}$. This is indeed very small! What it means is that the decay of $2s$ state going through the $2p$ state is possible, but this decay is limited by the slowness of $2s \to 2p$ transition and the two photon transition discussed above is far more important.

Finally, once you consider the spin of the electron (not required in this problem), the decay $2s_{1/2} \to 1s_{1/2}$ allows even parity $j = 1$ photon: an M1 transition. However, the M1 transition causes only the spin flip and does not change the spatial wave function at the leading order in kr. Hence the amplitude picks up higher order in the Taylor expansion in the spherical Bessel function $j_1(kr)$, which is $(kr)^3$ compared to kr of the leading term. Recall that the M1 is already one order higher in kr compared to the E1. Therefore there is an overall $(kr)^3$ suppression in the amplitude, and hence $(kr)^6$ in the rate compared to the E1 transition rate. Because $k \sim \alpha^2 mc/\hbar$ for the typical photon wave vector from the atomic transitions and $r \sim a_0 = \hbar/(\alpha mc)$, $kr \sim \alpha$. This leads to a factor of α^6 suppression in the rate relative to the E1 case, and hence negligible compared to the two-photon process.

In this decay, therefore, two photons are emitted promptly, giving vanishing total angular momentum. This is the ideal system for testing Einstein–Podolsky–Rosen paradox and Bell's inequality and had been used for that purpose.

Table 1: Comparison of Theoretical and Experimental Total Decay Rates of the $2s_{1/2}$ State (in s^{-1}). Taken from G.W.F. Drake, in "The Spectrum of Atomic Hydrogen Advances," edited by G. W. Series, World Scientific, 1988.

Ion	Theory	Experiment
He^+	526.61	525 ± 5
O^{7+}	2.1552×10^6	$(2.21 \pm 0.22) \times 10^6$
F^{8+}	4.3699×10^6	$(4.22 \pm 0.28) \times 10^6$
S^{15+}	1.3964×10^8	$(1.37 \pm 0.13) \times 10^8$
Ar^{17+}	2.8590×10^8	$(2.868 \pm 0.029) \times 10^8$

I could not find experimental data on the $2s$ lifetime for hydrogen, except the statement that it is very difficult to measure because of its too small decay rate (or too long lifetime). Instead, I found comparison between theory and data for hydrogen-like atoms. Following the analysis above with $Z > 1$, the two E1 photon emission process scales as Z^6, while one M1 photon emission as Z^{10}. At some point, the M1 emission catches up. Here is a table that compares theory and experiment. For Ar, the data is sufficiently accurate to be sensitive to the small M1 contribution of 0.0908×10^8 s^{-1}.