Notes on Atomic Structure
Friday, January 7, 2011

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1. Introduction

The study of the energy levels and transitions of atoms and one-atom ions is critical for understanding many features of the ISM:

- *Spectra*: Many of the strongest spectral lines from the ISM (both in UV/optical and FIR) are due to atoms and ions.
- *Thermal balance:* Excitation of atoms, followed by radiative decay, is a major cooling mechanisms for many ISM phases.

This lecture covers the energy level structure and radiative transition schemes of H, He, and the light metals. The transition metals are not covered due to their complexity, and also because most of the major lines we will be discussing are due to lighter elements, particularly C/N/O. The most abundant of the heavier metals is Fe, which we will discuss primarily in the context of dust (and in the case of X-ray processes where the inner electrons play a key role).

2. Hydrogen Atoms and One-Electron Ions

The ultimate reference for this material is Bethe & Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*.

A. BASIC STRUCTURE

Hydrogen is the simplest atom, consisting of a single electron and a nucleus. We will treat the hydrogenlike atoms generally, allowing for a nuclear charge Z. For example, $Z=2$ corresponds to the He$^+$ (He II) ion, whereas $Z=26$ corresponds to Fe^{25+} (Fe XXVI).

The atom can be treated by writing the Schrödinger equation for the single electron, with the potential

$$V(r) = -\frac{Ze^2}{r},$$

and the wave function can be separated in spherical coordinates as

$$\psi_{nlm_l}(r,\theta,\phi) = \frac{R_{nl}(r)}{r} Y_{lm_l}(\theta,\phi),$$

where Y is a spherical harmonic, R is the radial wave function, and nlm_l are quantum numbers. The angular quantum numbers are integers with $l\geq 0$, $|m_l|\leq l$.

Spherical symmetry guarantees that the different values of m have the same energy and the same radial wave function; this energy can be shown to be:

$$E_{nl} = -\frac{Z^2 e^4 m_e}{2\hbar^2 n^2} = -(13.6 \text{ eV})\frac{Z^2}{n^2},$$

where the radial wave functions have quantum numbers $n\geq l$. We note that due to an accidental degeneracy the different values of l for the same n have the same energy.

For a given value of (n,l) there are $2l+1$ possible wave functions, and for a given value of n there are n^2 wave functions (after including all legal values of l). To account for electron spin (up or down; $m_s=\pm\frac{1}{2}$), the number of states should be doubled to $2(2l+1)$ or $2n^2$.

The ground state of H is $n=1$, which has only one wave function (and two spin states).

The angular momentum number l is frequently denoted with a letter: s ($l=0$), p ($l=1$), d($l=2$), f ($l=3$), g ($l=4$), etc. Thus the ground state is 1s.

B. RADIATIVE TRANSITIONS

Radiation can be emitted by an atom in an excited state with a frequency ν given by

$$h\nu = E - E',$$

where E is the energy of the upper level and E' is that of the lower level. For a hydrogenlike atom, the frequencies are then given by

$$\nu = \frac{13.6 \text{ eV}}{h} Z^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right),$$

where $n_2 < n_1$ are positive integers.

The transition wavelengths for the hydrogen atom are:

Lyman series ($n_2=1$)		
Lyα	2 → 1	1216 Å
Lyβ	3 → 1	1026 Å
Lyγ	4 → 1	973 Å
Lyδ	5 → 1	950 Å

Paschen series ($n_2=3$)		
Paα	4 → 3	1.875 μm
Paβ	5 → 3	1.282 μm
Paγ	6 → 3	1.094 μm
Paδ	7 → 3	1.005 μm

Balmer series ($n_2=2$)		
Hα	3 → 2	6563 Å
Hβ	4 → 2	4861 Å
Hγ	5 → 2	4340 Å
Hδ	6 → 2	4102 Å

Brackett series ($n_2=4$)		
Brα	5 → 4	4.05 μm
Brβ	6 → 4	2.63 μm
Brγ	7 → 4	2.17 μm
Brδ	8 → 4	1.95 μm

In our studies, we will also want to know the rate of emission of photons (the radiative decay rates). A correct calculation requires QED, but we may estimate the decay rate semi-classically. In classical physics (Ph 1c), the rate at which energy is emitted from an electric dipole of moment **μ** is:

$$P = \frac{2\ddot{\mu}^2}{3c^3} = \frac{2\omega^4 \mu^2}{3c^3}.$$

If we think of this power as being emitted in discrete units of energy $\hbar\omega$, the rate of emission of photons Γ (with units of counts per second) is

$$\Gamma = \frac{2\omega^3 \mu^2}{3\hbar c^3}.$$

For a given transition, we know $\omega = 2\pi\nu$, but we do not yet know the dipole moment μ. We do know the expectation value of the dipole moment for a superposition of the initial and final states ψ_1 and ψ_2:

$$\psi(\mathbf{x}) = c_1\psi_1(\mathbf{x}) + c_2\psi_2(\mathbf{x}),$$

$$\mu = -e\langle \mathbf{x} \rangle = -e|c_1|^2 \langle \psi_1 | \mathbf{x} | \psi_1 \rangle - e|c_2|^2 \langle \psi_2 | \mathbf{x} | \psi_2 \rangle - 2e\,\text{Re}\left(c_2^* c_1 \langle \psi_2 | \mathbf{x} | \psi_1 \rangle \right).$$

Now we note that the initial and final wave functions have definite parity, that is, $\psi(\mathbf{x}) = \pm\psi(-\mathbf{x})$. In the case of hydrogen, the + parity applies to even l and the − to odd l. The situation will be more complicated for heavier atoms, but the wave functions will still have definite parity (i.e. when the coordinates of all electrons are sign-reversed, the overall wave

function has a + or − sign) since the parity operation commutes with the Hamiltonian. This implies that $\langle\psi_1|\mathbf{x}|\psi_1\rangle=0$, so only the overlap integral contributes to μ. Thus the classical emission rate is

$$\Gamma = \frac{8\omega^3 e^2}{3\hbar c^3}\left[\mathrm{Re}\left(c_2^* c_1 \langle\psi_2|\mathbf{x}|\psi_1\rangle\right)\right]^2.$$

Now we know from elementary quantum mechanics that $c_j \propto \exp(-iE_j t/\hbar)$, so in the above the real part is oscillating as a function of time and the square of the real part averages to ½ of the square of the absolute value. One might guess that during a radiative transition, both c_1 and c_2 are of order unity. In fact, this argument is correct: the exact QED result is

$$\Gamma = \frac{4\omega^3 e^2}{3\hbar c^3}\left|\langle\psi_2|\mathbf{x}|\psi_1\rangle\right|^2.$$

In most practical cases, we are interested in the total decay rate to all m-sublevels of the final state. This decay rate is often called the Einstein A-coefficient and symbolized by A_{12}:

$$A_{12} = \frac{4\omega^3 e^2}{3\hbar c^3}\sum_{m_2=-l_2}^{l_2}\left|\langle\psi_{2,m_2}|\mathbf{x}|\psi_1\rangle\right|^2.$$

Note that transitions are only allowed if they flip parity (otherwise the matrix element is zero by symmetry). This is an example of a **selection rule**. For hydrogen, this means l_2-l_1 is odd.

For the case of hydrogen, the A coefficients can be determined exactly. We separate the matrix element into radial and angular pieces:

$$\langle\psi_2|\mathbf{x}|\psi_1\rangle = \int_0^\infty r R_{n_2 l_2}^*(r) R_{n_1 l_1}(r)\,dr \int_{S^2}\hat{\mathbf{n}}Y_{l_2 m_2}^*(\hat{\mathbf{n}})Y_{n_1 l_1}(\hat{\mathbf{n}})\,d^2\hat{\mathbf{n}}.$$

The integral involving the spherical harmonic is only nonzero if $l_2-l_1=\pm1$ (the triangle inequality for angular momentum forbids larger changes; alternatively, write Y_{lm} as a polynomial of order l in the Cartesian components of $\mathbf{n}$ and observe that $\mathbf{n}Y_{lm}$ is a polynomial of order $l+1$, hence must be composed exclusively of spherical harmonics of order $\le l+1$). This is a general rule.

For the allowed transitions and small values of n, the matrix element is of order the Bohr radius (10^{-8} cm), the angular frequencies are of order 10^{16}/s, and so we get decay rates of the order of 10^9/s (lifetimes $\sim$ 1ns). This is indeed correct. Actual calculations give the following rates (in units of 10^9/s):

2p → 1s	0.625		
3s → 2p	0.0063		
3p → 1s	0.164	3p → 2s	0.022
3d → 2p	0.064		

4s → 2p	0.0025	4s → 3p	0.0018		
4p → 1s	0.068	4p → 2s	0.0095	4p → 3s	0.0030
		4p → 3d	0.0003		
4d → 2p	0.0204	4d → 3p	0.0070		
4f → 3d	0.0137				

For heavier atoms, the transition frequencies scale as $\omega \propto Z^2$, the radii scale as $1/Z$, and so the transition rates scale as Z^4, e.g. they are 16× larger for He II than for H I.

One notable feature of the above is that the 2s level of hydrogen cannot decay: the only lower energy level is 1s, and the parity selection rule forbids this. The 2s level instead decays by **two-photon decay**:

$$H(2s) \rightarrow H(1s) + \gamma + \gamma.$$
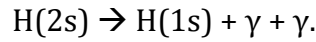
The *sum* of the energies of the two emitted photons is $E_{2s} - E_{1s}$ = 10.2 eV. The photons have a continuous spectrum since there is no other constraint on their energies. This is a major contributor to the UV/optical continuum from many nebulae.

Quantum mechanically, this corresponds to emitting one photon and landing in an intermediate 2p state, and then emitting the second photon. The uncertainty principle allows the hydrogen atom to "borrow" the energy to emit the first photon, for a period of time of order $\Delta t \sim \hbar / \Delta E \sim 10^{-16}$s. Semi-classically, we would expect the rate coefficient for 2s decay to be of order 10^9/s, multiplied by the probability for the 2p state to decay within 10^{-16} s, i.e. 10^{-7}. This calculation gives 10^{-2}/s. It is in fact correct to an order of magnitude. The rate coefficient for this process is $8.2Z^6$/s, so the lifetime of the 2s state in hydrogen is 0.12 s.

Excited states with unusually long lifetimes due to the absence of allowed decays (with nonzero dipole moments) are said to be **metastable**.

C. ELECTRON SPIN & FINE STRUCTURE

So far we have treated the electron spin as an unimportant auxiliary variable. However in some cases, particularly for heavier atoms, it matters.

We can define the total angular momentum of the electron by the vector sum of its orbital and spin angular momenta, **j** = **l** + **s**. This is important because when we account for the magnetic moment of the electron, it is the total angular momentum that is conserved and hence j, m_j represent good quantum numbers. For given values of n and l, and recalling that the electron has spin $s = \frac{1}{2}$, we can then use the triangle inequality to write the possible values of j:

$$j = l \pm \tfrac{1}{2}.$$

(If $l = 0$, the − sign is forbidden.) There is also a projection of **j** onto the z-axis, the magnetic quantum number m_j:

$$m_j = m_l + m_s.$$

Since the number of possible values of m_j is $2j+1$, we can see that the total number of states for a given (n,l), the total number of quantum states is:

$$g_{nl} = [2(l - \tfrac{1}{2}) + 1] + [2(l + \tfrac{1}{2}) + 1] = 2(2l + 1),$$

as found before.

We now come to the question of the energy of these levels, and in particular whether the Rydberg formula $E \sim -1/n^2$ receives any corrections associated with the electron spin. We can estimate at order of magnitude level the energy associated with the magnetic moment by supposing that the electron sees a semiclassical magnetic field,

$$\mathbf{B} = \frac{\mathbf{E} \times \mathbf{v}}{c} = \frac{Ze}{cr^2}\hat{\mathbf{r}} \times \mathbf{v} = \frac{Ze}{m_e cr^3}\mathbf{l}.$$

Since the electron's magnetic moment is $-e\mathbf{s}/m_e c$, the energy of interaction is:

$$\Delta E = \frac{Ze^2}{m_e^2 c^2 r^3}\mathbf{l} \cdot \mathbf{s}.$$

For a low-lying state, the typical value for the radius is $r \sim a_0/Z$, where $a_0 = \hbar^2/m_e e^2$ is the Bohr radius. The orbital and spin angular momenta are $\sim \hbar$. So the correction to the energy is, at order of magnitude level,

$$\Delta E = \frac{Z^4 m_e e^8}{c^2 \hbar^4}.$$

This is of order $\sim (Z\alpha)^2$ times the Schrödinger equation energy, where α is the **fine structure constant**:

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}.$$

In fact, the semiclassical velocity of an electron in the first Bohr orbit is $Z\alpha c$, so we might expect relativistic corrections to be important at the same level; they are. All of the order-α^2 corrections result in a perturbation to the Schrödinger equation energies known as **fine structure** corrections. The full result is

$$E_{nlj} = -\frac{Z^2 e^4 m_e}{2\hbar^2 n^2}\left[1 + \frac{Z^2 \alpha^2}{n^2}\left(\frac{n}{j + \tfrac{1}{2}} - \frac{3}{4}\right)\right].$$

The lower-j levels have lower energy, as one would expect since **l•s** is negative. To this order in perturbation theory, the levels with different l but the same j have the same energy; for example, in the case of $n=2$, there are three levels:

$nl_j =$ $2s_{1/2}$ (degeneracy 2)
            $2p_{1/2}$ (degeneracy 2)
            $2p_{3/2}$ (degeneracy 4).

The first two have the same energy and $2p_{3/2}$ has higher energy (by 45 μeV). In full QED, the $2s_{1/2}$ level actually has slightly higher energy than $2p_{1/2}$ by 4 μeV due to loop corrections (which we won't need to discuss in this class).

     The fine structure effects are small on account of $\alpha \ll 1$, and for hydrogen itself are usually unimportant in the ISM. Nevertheless, they can be very important for two reasons:

- *Metals*: The fractional effect of fine structure scales as Z^2, so for metals the spectral lines can actually be resolved into multiple fine structure components. The ratios of these lines are an important diagnostic.
- *Cooling*: In hydrogen, the ground state has only one fine structure component, $1s_{1/2}$. However for metals it is often the case that the ground state splits into two components. In cold gas, one can collisionally excite the metal atom from its true ground state into the fine-structure excited state. When the atom radiatively decays to the ground state, it emits energy, thereby cooling the gas. Fine structure cooling is dominant in some phases of the ISM.

D. HYPERFINE STRUCTURE

     Although the $n=1$ level hydrogen atom has only one component, $1s_{1/2}$, when considering only the electron, this is split when taking into account that the proton has spin $I=\frac{1}{2}$. The combination of the electron and proton-spin angular momentum gives us the total angular momentum of the atom, **F** = **j** + **I**. Since $j=\frac{1}{2}$ in the $1s_{1/2}$ level, we may have either $F=0$ or $F=1$, with degeneracies $2F+1$. The interaction of the proton and electron magnetic moments splits these energy levels: $F=0$ is lower than $F=1$. The difference is

$$\Delta E_{10} = \frac{2\mu_e \mu_p}{a_0^3} = 5.9 \ \mu eV \,.$$

The existence of a splitting between the $F=0$ and 1 levels brings up the question of the lifetime of the $F=1$ level. Since both levels have positive parity, the electric dipole matrix element is zero and $F=1$ is metastable. The excited state can however decay by magnetic dipole radiation (due to the magnetic moment of the electron), with rate

$$\Gamma = \frac{4\omega^3}{3\hbar c^3} \left| \langle \psi_{F=0} | \mu_e | \psi_{F=1} \rangle \right|^2 \,.$$

This corresponds to a lifetime of 10 Myr. The photon frequency is 1.4 GHz and its wavelength is 21 cm. This hydrogen line is thus in the radio, and it has played a key role in our understanding of the structure of the Milky Way and nearby galaxies.

Spectral lines with no contribution from the electric dipole moment are described as **forbidden** and are denoted with brackets, in this case [H I] λ21cm. This distinguishes them from **allowed** transitions with no brackets, e.g. Hα, which we would denote as H I λ6563Å.

3. Helium Atoms and Two-Electron Ions

A. DESCRIPTION OF MULTI-ELECTRON ATOMS

We now consider two-electron atoms. In general, for multi-electron atoms, we will introduce the following notation. Lower-case letters l, s, j will denote the quantum numbers for an individual electron, whereas capital letters L, S, J will denote angular momenta for the sum of all electrons.

We will use the **term symbol** for an atomic level to describe its overall symmetry properties. Specifically, we write:

$$^{2S+1}L_J^P,$$

where the parity P is either even (e) or odd (o); the orbital angular momentum is specified with a letter (e.g. S for L=0, P for L=1, etc.); and $2S$+1 is an integer. An atom is described by its **electron configuration** (occupation of each type of orbital), its term symbol, and possibly additional information to uniquely identify the level (usually required only for complicated atoms such as the transition metals or rare earths). For example, a hydrogen atom in the ground (1s$_{1/2}$) state has a term symbol $^2S_{1/2}^e$, whereas in the 2p$_{3/2}$ level the term symbol is $^2P_{3/2}^o$.

In these notes, we will keep the parity in all cases, but many authors (including Osterbrock & Ferland) only write the o for odd parity and leave the parity field blank for even parity.

The transitions between different energy levels are governed by selection rules. The selection rules for our most common types of transitions are:

Electric dipole:
    Exact: ΔJ=−1, 0, or +1 (no 0→0);   opposite parity
    Approximate: ΔL=−1, 0, or +1 (no 0→0); ΔS=0.

Magnetic dipole:
    Exact: ΔJ=−1, 0, or +1 (no 0→0);   same parity
    Approximate: ΔL=ΔS=0; same configuration.

Electric quadrupole:
    Exact: $|\Delta J|$≤2 (no 0→0, 0→1, or 1→0); same parity
    Approximate: $|\Delta L|$≤2 (no 0→0, 0→1, or 1→0); ΔS=0.

Most of these are determined by the triangle inequality and by the requirement that the integral for the matrix element be even under parity (so that it doesn't cancel). The exception is the magnetic dipole moment operator, which is unusual because the operators **L** and **S** correspond to infinitesimal rotations of the orbital and spin wave functions. "Approximate" rules depend on the fact that for non-relativistic wave functions **L** and **S** commute with the Hamiltonian.

B. ENERGY LEVEL STRUCTURE

The energy levels of the helium atom are governed by two effects. One is the Pauli exclusion principle, which tells us that the overall wave function must be antisymmetric under interchange of the two electrons. That is,

$$\Psi(\mathbf{x}_1,\tau_1,\mathbf{x}_2,\tau_2) = -\Psi(\mathbf{x}_2,\tau_2,\mathbf{x}_1,\tau_1),$$

where τ denotes the spin degree of freedom of each electron. The second is the repulsion between the two electrons, which in quantum mechanics can manifest itself in an unconventional way. The nonrelativistic Hamiltonian for a heliumlike ion of atomic number Z is:

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}.$$

Now we can see that the spin wave functions are not affected by the Hamiltonian, so we may separate the orbital and spin variables:

$$\Psi(\mathbf{x}_1,\tau_1,\mathbf{x}_2,\tau_2) = \Psi_{orb}(\mathbf{x}_1,\mathbf{x}_2)\Psi_{spin}(\tau_1,\tau_2).$$

Since the overall wave function is to be antisymmetric, we may consider two possibilities:

- **Singlets** or para-helium: here the orbital wave function is symmetric and the spin wave function is antisymmetric. Since the spin choices for an individual electron are $\uparrow(\tau)$ and $\downarrow(\tau)$, the only antisymmetric choice is

$$\Psi_{spin}(\tau_1,\tau_2) = \frac{1}{\sqrt{2}}[\uparrow(\tau_1)\downarrow(\tau_2) - \downarrow(\tau_1)\uparrow(\tau_2)],$$

  which has spin $S=0$ and z-component $M_S=0$.
- **Triplets** or ortho-helium: the orbital wave function is antisymmetric and the spin wave function is symmetric. There are three possible spin wave functions:

$$\Psi_{\text{spin}}(\tau_1,\tau_2) = \uparrow(\tau_1)\uparrow(\tau_2),$$

$$\Psi_{\text{spin}}(\tau_1,\tau_2) = \frac{1}{\sqrt{2}}[\uparrow(\tau_1)\downarrow(\tau_2) + \downarrow(\tau_1)\uparrow(\tau_2)],,$$

$$\Psi_{\text{spin}}(\tau_1,\tau_2) = \downarrow(\tau_1)\downarrow(\tau_2),$$

which have spin $S=1$ and z-component $M_S=1,0,-1$.

The lowest energy level of helium should correspond to the $1s^2$ configuration, i.e. placing both electrons in the lowest energy orbital. This requires a symmetric wave function, so it must be a singlet state. It thus has orbital angular momentum zero, spin zero, and even parity, so we write it as:

$$1s^2 \; {}^1S_0^e.$$

In the absence of repulsion between the two electrons, its energy would be twice the energy of the $n=1$ level of the He^+ ion, i.e. -108.8 eV. In reality, the electrons repel each other, so the total energy ends up being higher, -79.0 eV. The **ionization energy** – the energy required to remove one electron – is then -24.6 eV (the difference between this energy and that of He^+).

The somewhat higher energy levels of helium have one electron in the 1s orbital and one in a higher orbital, $1snl$ ($n\geq 2$). These can be either singlet or triplet because the orbital wave function can be either symmetric or asymmetric. To a first approximation, the energies can be treated by supposing that the nucleus and 1s electron form a He^+ "core" around which the nl electron orbits, i.e.:

$$E_{1snl} \approx -(13.6 \text{ eV})\left(4 + \frac{1}{n^2}\right).$$

However, particularly for small n and l, there is a correction due to the fact that the outer electron occasionally penetrates into the core. This results in two effects. First, because the second electron sees a higher nuclear charge, the energy levels are lowered, particularly for the $1sns$ states (recall that the s wave functions are the ones that are nonzero at the origin). Secondly, if we approximate the wave function as

$$\Psi_{\text{orb}}(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}[\psi_{1s}(\mathbf{x}_1)\psi_{nl}(\mathbf{x}_2) \pm \psi_{nl}(\mathbf{x}_1)\psi_{1s}(\mathbf{x}_2)],$$

then the electron-electron repulsion term is slightly more effective for the + sign (singlet) than the – sign (triplet). This **exchange interaction** causes the singlet energy levels to be slightly above the triplet energy levels. The general fact that larger values of S have lower energy (for the same configuration) is called **Hund's first rule**.

The orbital angular momentum L of the $1snl$ levels is simply l, and the parity is even or odd according to whether l is even or odd.

It is possible to have doubly-excited states of helium, e.g. 2s2p. These states actually have more energy than a He$^+$ ion and a free electron. Therefore they are unstable and **auto-ionize**:

$$\text{He}(2s2p) \rightarrow \text{He}^+(1s) + e^-.$$
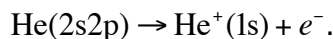
We therefore usually don't observe spectral lines from these states (in fact the short auto-ionization lifetime and the uncertainty principle $\Delta E \Delta t \geq \hbar/2$ usually make such lines very broad). But we will need to consider them when we discuss ionization and recombination processes, particularly for metals.

Finally, the triplet levels ($S=1$) with $L>0$ have fine structure: the total angular momentum can add up to $J=L-1$, L, or $L+1$.

We may now summarize the energies of the helium atom for the configurations up through 1s2l:[1]

Configuration	Spin	Configuration + Term	Energy (eV) [relative to He$^+$]
1s2p	Singlet	1s2p $^1P^o_1$	−3.36937 eV
	Triplet	1s2p $^3P^o_0$	−3.62317 eV
		1s2p $^3P^o_1$	−3.62329 eV
		1s2p $^3P^o_2$	−3.62330 eV
1s2s	Singlet	1s2s $^1S^e_0$	−3.97161 eV
	Triplet	1s2s $^3S^e_1$	−4.76777 eV
1s^2	Singlet	1s^2 $^1S^e_0$	−24.58739 eV

C. RADIATIVE TRANSITIONS

We now come to the radiative transitions in the helium atom. It is easily seen that there can be no allowed transitions between singlet and triplet states (we will come back to this later). Within the singlet and triplet schemes, the types of transitions are similar to those of hydrogen, with the He$^+$ core being a spectator. The main exceptions are that (i) the triplets don't have a 1s^2 level, so there is no triplet analogue of the Lyman series; (ii) the different energy levels due to different l values causes the Balmer-like series of helium to be split into many more lines; and (iii) because the 1s2s levels are below the 1s2p levels, decays of the form 1s2p → 1s2s are now possible.

The most notable of the allowed He I transitions are:

Analogue of Lyman-α: $1s2p\ ^1P^o_1 \rightarrow 1s^2\ ^1S^e_0$ 584 Å

Analogues of Hα: $1s3p\ ^3P^o_{0,1,2} \rightarrow 1s2s\ ^3S^e_1$ 3889 Å

                             $1s3p\ ^1P^o_1 \rightarrow 1s2s\ ^1S^e_0$ 5015 Å

[1] Energies are from the NIST database,
http://physics.nist.gov/PhysRefData/ASD/index.html

$$1s3d\ ^3D^e_{1,2,3} \rightarrow 1s2p\ ^3P^o_{0,1,2} \qquad 5876\ \text{Å}$$
$$1s3d\ ^1D^e_2 \rightarrow 1s2p\ ^1P^o_1 \qquad 6678\ \text{Å}$$
$$1s3s\ ^3S^e_1 \rightarrow 1s2p\ ^3P^o_{0,1,2} \qquad 7065\ \text{Å}$$
$$1s3s\ ^1S^e_0 \rightarrow 1s2p\ ^1P^o_1 \qquad 7281\ \text{Å}$$

"New" 2p → 2s lines:
$$1s2p\ ^3P^o_{0,1,2} \rightarrow 1s2s\ ^3S^e_1 \qquad 10830\ \text{Å}$$
$$1s2p\ ^1P^o_1 \rightarrow 1s2s\ ^1S^e_0 \qquad 20587\ \text{Å}$$

The helium atom has two metastable levels with no allowed decays: the singlet and triplet of 1s2s. The $1s2s\ ^1S^e_0$ level decays in a way similar to that for hydrogen 2s, with a lifetime of 0.02 s:

$$\text{He}(1s2s\ ^1S^e_0) \rightarrow \text{He}(1s^2\ ^1S^e_0) + \gamma + \gamma.$$

The $1s2s\ ^3S^e_1$ level cannot decay via conventional two-photon emission since such a process does not change the electron spin. It should not decay by magnetic dipole emission either because the magnetic dipole moment operator,

$$\mu = \frac{e}{2m_e c}(\mathbf{L} + 2\mathbf{S}),$$

cannot change the value of S. In reality it is possible for such a decay to occur because of (i) relativistic corrections to the wave functions, and (ii) corrections to the dipole emission formula from the finite size of the atom.[2] This endows metastable triplet helium with a finite lifetime of 2 hours (!). This shortens as $\sim Z^{10}$ for heavy ions. In fact, the $1s2s\ ^3S^e_1 \rightarrow 1s^2\ ^1S^e_0$ decays were observed in the solar corona for [C V] λ42Å and the appropriate lifetime (0.03 s) derived, before the correct theory was developed.

4. The Light Metals

We are now ready to consider the energy level structure of light metals. For the most part, we will focus our attention on the lowest several electronic configurations, which are of the greatest astrophysical importance, both for cooling and for UV absorption line studies. We will organize the discussion according to the number of valence electrons, as this determines the organization of the energy level diagram.

The line information here is from the NIST database.

A. ONE VALENCE ELECTRON

We consider first the case of 1 valence electron (i.e. total number of electrons 3, 11, or 19). Important examples include many of the species responsible for ISM and IGM

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[2] See Drake, Phys. Rev. A 3, 908 (1971) for a discussion of these points.

absorption lines (C IV, N V, O VI, Na I, Mg II, Al III, Si IV, Ca II); and some (C IV, O VI, Ne VIII, etc.) are also important to the cooling of hot gas.

   Such an atom has its lowest orbitals filled, and one electron available in the valence shell. Examples of ground states are:

- Lithium-like: $1s^2 2s$
- Sodium-like: $1s^2 2s^2 2p^6 3s$
- Potassium-like: $1s^2 2s^2 2p^6 3s^2 3p^6 4s$

We will simply denote these by ns, where n=2, 3, or 4, and the inner electrons are implied.
   For n=2 and n=3, the two lowest configurations for one-valence-electron atoms are usually ns and np; the np level is fine-structure-split into a J=1/2 and a J=3/2 level. Thus, the term symbols are:

$$n\text{s }^2\text{S}^e_{1/2} \text{ (ground)}, \; n\text{p }^2\text{P}^o_{1/2}, \text{ and } n\text{p }^2\text{P}^o_{3/2}.$$

The np → ns decays are allowed by all symmetries. Moreover, they tend to have relatively low frequencies (optical or near UV) because the energy splitting between ns and np is relatively small.
   The table shows the transitions for the major one valence electron ions. For continuity we show the sequence of consecutive elements even though some (Li, Be, B, F) are too rare to be of significance in the ISM. Note that the fine structure splitting becomes more important for higher Z. Also note the "doublet" structure: these ions tend to have a pair of lines at very closely spaced wavelengths.

n	Atom or Ion	Wavelength of np ^{2}P$^o_{1/2}$ → ns ^{2}S$^e_{1/2}$ (Å)	Wavelength of np ^{2}P$^o_{3/2}$ → ns ^{2}S$^e_{1/2}$ (Å)
2	Li I	6707.9	6707.8
	Be II	3131.1	3130.4
	B III	2067.2	2065.8
	C IV	1550.8	1548.2
	N V	1242.8	1238.8
	O VI	1037.6	1031.9
	F VII	890.8	883.1
	Ne VIII	780.3	770.4
3	Na I	5895.9	5890.0
	Mg II	2802.7	2795.5
	Al III	1862.8	1854.7
	Si IV	1402.8	1393.8
4	K I	7699.0	7664.9
	Ca II	3968.5	3933.7

For Ca II, there is an additional set of levels, $3d\ ^2D^e_{3/2,5/2}$, which lie at a lower energy than $4p\ ^2P^o_{1/2,3/2}$. We will not concern ourselves with them in this class.

B. TWO VALENCE ELECTRONS

We now move to the case of two valence electrons (e.g. total number of electrons 4 or 12). Like the case of the helium atom, the two valence electrons can form a spin singlet or triplet. The ground state has both valence electrons in the 2s (or 3s) orbital, and hence must be a singlet. Thus we have the ground term $ns^2\ ^1S^e_0$, where n=2 (4 electrons) or n=3 (12 electrons).

The lowest excitations will promote one electron to np. According to Hund's first rule, the triplet $ns n$p levels will lie below the singlet. Thus the ordering of the first three sets of energy levels is:

$ns n$p $^1P^o_1$ 2nd excited; decays to ground

$ns n$p $^3P^o_{0,1,2}$ 1st excited; metastable

$ns^2\ ^1S^e_0$ ground

The triplet states cannot decay to the ground state on account of the change in S. However, for the case of $ns n$p $^3P^o_1$, the angular momentum and parity are appropriate for an electric dipole moment matrix element. This results in the decay being only **semi-forbidden**: relativistic corrections that mix $ns n$p $^3P^o_1$ with $ns n$p $^1P^o_1$ allow $ns n$p $^3P^o_1$ to decay radiatively. Semi-forbidden transitions are denoted with a one-sided bracket, e.g. C III] λ1909Å.

Ion	Allowed decay $ns n$p $^1P^o_1 \rightarrow ns^2\ ^1S^e_0$		Semi-forbidden decay $ns n$p $^3P^o_1 \rightarrow ns^2\ ^1S^e_0$	
	Wavelength	**Rate**	**Wavelength**	**Rate**
C III	977 Å	1.8/ns	1909 Å	110/s
N IV	765 Å	2.3/ns	1486 Å	600/s
O V	629 Å	2.8/ns	1218 Å	2300/s
Si III	1207 Å	2.6/ns	1892 Å	

The $ns n$p $^3P^o_{0,2}$ levels have alternative decay paths, e.g. electric quadrupole decays to the ground state (for J=2) and two-photon decay (for J=0). However, in most cases collisions are a more important means of de-populating these states.

C. THE P-BLOCK ATOMS

We now come to the atoms with partially filled p sublevels. These will be extremely important for the spectra and thermal balance of H II regions. Our principal concern will be with the ground electron configurations.

The p sublevel (either 2p or 3p) can accommodate up to six electrons. Therefore the partially filled levels consist of:

np^1 atoms: C II, N III, O IV, Si II, S IV
np^2 atoms: C I, N II, O III, Ne V, Si I, S III, Ar V
np^3 atoms: N I, O II, Ne IV, S II, Ar IV
np^4 atoms: O I, Ne III, S I, Ar III
np^5 atoms: Ne II, Ar II

Since every p wave function has negative parity, the overall parity of the np^k configuration is $(-1)^k$.

The ordering of energy levels is given by Hund's rules. We already encountered the first rule (that the largest S has the lowest energy for a given configuration). We will now need:

- **Hund's second rule**: For a given configuration and value of S, the largest orbital angular momentum L corresponds to the lowest energy.
- **Hund's third rule**: For a given configuration, S, and L, the lowest energy corresponds to the lowest J for less than half-filled subshells (np^1 or np^2), and the highest J for more than half-filled subshells (np^4 or np^5).

Let's explore how these rules work.

$$n\text{p}^1$$

For the np^1 atoms, there is only one electron in the p subshell, so we must have $S=1/2$ and $L=1$. Therefore Hund's third rule tells us that the ground level is np $^2\mathrm{P}^o_{1/2}$, and there is a fine structure excited level, np $^2\mathrm{P}^o_{1/2}$. The total number of quantum states is 2+4=6, in accordance with the number of p spin-orbitals. The energy splitting between these states is small (typically of order a few milli-eV) since it is due to fine structure. The transition between these two states must be a magnetic dipole transition since there is no change in parity. The key transitions of this type have wavelengths:

[C II]   158 μm   [N III] 57 μm   [O IV] 25.9 μm
[Si II] 34.8 μm   [S IV] 10.5 μm

The magnetic dipole moments are all equal (since the operator only depends on angular momentum) so the lifetimes scale as $\propto \lambda^3$. For C II, the lifetime is 5 days. These lifetimes allow a significant abundance of excited ions to persist in the ISM.

$$n\text{p}^2$$

Now there are two electrons in the p subshell, so we may have the electron spins either symmetric ($S=1$) or antisymmetric ($S=0$). Hund's rules tell us that $S=1$ will have lower energy; this corresponds to antisymmetric orbital wave functions. With the three p orbitals (x, y, and z), there are 3 antisymmetric combinations:

$$\Psi_x = 2^{-1/2}[\psi_y(1)\psi_z(2) - \psi_z(1)\psi_y(2)]$$
$$\Psi_y = 2^{-1/2}[\psi_z(1)\psi_x(2) - \psi_x(1)\psi_z(2)].$$
$$\Psi_z = 2^{-1/2}[\psi_x(1)\psi_y(2) - \psi_y(1)\psi_x(2)]$$

These have the same rotational properties as a vector (the cross product!) so they have $L=1$. The triangle inequality then says we may have $J=0$, 1, or 2. Using Hund's third rule, we establish the ordering of energies: $J=0$ is the ground state.

  If the atom is excited, it may have $S=0$. Then the orbital wave function must be symmetric. The possible values of L are then either 0 or 2 (we know from the triangle inequality that since the individual electrons have $l=1$, the possible values of L are 0, 1, and 2; and we have just seen that 1 is antisymmetric). For example, $L=0$ corresponds to:

$$\Psi_{L=0} = 3^{-1/2}[\psi_x(1)\psi_x(2) + \psi_y(1)\psi_y(2) + \psi_z(1)\psi_z(2)].$$

Thus we have two possibilities: $L=2$ (implying $J=2$) has lower energy, and $L=0$ ($J=0$) has higher energy. The energy levels within the np^2 configuration are thus ordered as:

$$^3P_0^e < {}^3P_1^e < {}^3P_2^e < {}^1D_2^e < {}^1S_0^e.$$

We may check that the total number of quantum states is

$$5 + 3 + 1 + 5 + 1 = \binom{6}{2} = 15.$$

The np^2 atom supports several types of transitions. These include the fine structure transitions within the $^3P_{0,1,2}^e$ system, analogous to those of np^1. The excited terms $^1D_2^e$ and $^1S_0^e$ can decay via magnetic dipole or electric quadrupole decays. All decays from $^1D_2^e$ do violate the approximate selection rules, which endows $^1D_2^e$ with an unusually long lifetime.
  The transition wavelengths are:

Decay:	Type	[N II]	[O III]	[S III]
$^1S_0^e \rightarrow {}^1D_2^e$	El. Quad.	5755 Å	4363 Å	6312 Å
$^1D_2^e \rightarrow {}^3P_1^e$	Mag. Dipole	6548 Å	4959 Å	9069 Å
$^1D_2^e \rightarrow {}^3P_2^e$	Mag. Dipole	6583 Å	5007 Å	9531 Å
$^3P_2^e \rightarrow {}^3P_1^e$	Mag. Dipole	122 μm	52 μm	18.7 μm
$^3P_1^e \rightarrow {}^3P_0^e$	Mag. Dipole	205 μm	88 μm	33.4 μm

In O III, the lifetimes are 11 hrs ($^3P_1^e$), 3 hrs ($^3P_2^e$), 40 s ($^1D_2^e$), and 0.6 s ($^1S_0^e$).

$$n\text{p}^3$$

We next consider having three p electrons. There are now

$$\binom{6}{3} = 20$$

quantum states available. Our job is to find them all.

We first identify the ground state, which will have the maximum spin S. With three electrons, this is achieved by taking $S=3/2$ (remember the triangle inequality!), which is a purely symmetric spin wave function. The orbital wave function must then be purely antisymmetric. The only purely antisymmetric combination of 3 orbitals is:

$$\Psi_{orb}(1,2,3) = 6^{-1/2}[\psi_x(1)\psi_y(2)\psi_z(3) + \psi_y(1)\psi_z(2)\psi_x(3) + \psi_z(1)\psi_x(2)\psi_y(3)$$
$$- \psi_x(1)\psi_z(2)\psi_y(3) - \psi_y(1)\psi_x(2)\psi_z(3) - \psi_z(1)\psi_y(2)\psi_x(3)].$$

It is rotationally invariant and thus has $L=0$. We then have $J=3/2$ and the ground level is $^4S^o_{3/2}$.

This identifies 4 of the states. The other 16 must have $S=1/2$, and be of mixed symmetry (i.e. the spin and orbital wave functions are neither symmetric nor antisymmetric, only the overall wave function is antisymmetric). The triangle inequality tells us that they can only have $L=0$, 1, 2, and 3. But they cannot have $L=3$ since this would imply a purely symmetric orbital wave function (and there is no purely antisymmetric spin wave function with 2 spin states and 3 electrons); and $L=0$ can have only the wave function we already described. Noting that a given L and S imply $(2S+1)(2L+1)$ quantum states, combinatorics tells us that we must have one $L=1$ set of levels and one $L=2$. Hund's rules then give us the ordering (except for fine structure, which is determined either empirically or via more detailed calculation):

$$^4S^o_{3/2} < {}^2D^o_{5/2} < {}^2D^o_{3/2} < {}^2P^o_{1/2} < {}^2P^o_{3/2}.$$

The most important transitions are the forbidden doublet transitions from $^2D^o_{3/2,5/2} \rightarrow {}^4S^o_{3/2}$. Its wavelengths are:

N I   5198, 5200 Å
O II   3726, 3729 Å
S II   6716, 6731 Å

Lifetimes of $^2D^o_{3/2,5/2}$ range from tens of minutes to days.

Because the ground term has $S=0$, there are no fine structure lines of the $n\text{p}^3$ ions.

$$n\text{p}^4$$

The np^4 ions appear at first glance that they might be even more complicated to investigate. However, it is profitable to think of them as being noble gases with two missing electrons, or **holes**. The hole has the same orbital angular momentum ($l=1$) and spin ($s=\frac{1}{2}$) as the electron, and obeys the Pauli exclusion principle (it is nonsense to have two holes in the same quantum state). But we have already solved the two-electron (np^2) problem, so we may use the same solution for the holes. The exception is that in accordance with Hund's third rule, the fine structure ordering is reversed.

$$^3P^e_2 < {}^3P^e_1 < {}^3P^e_0 < {}^1D^e_2 < {}^1S^e_0.$$

The transition wavelengths are:

Decay:	Type	[O I]	
$^1S^e_0 \rightarrow {}^1D^e_2$	El. Quad.	5577 Å	[Also observed from Earth's atmosphere!]
$^1D^e_2 \rightarrow {}^3P^e_2$	Mag. Dipole	6300 Å	
$^1D^e_2 \rightarrow {}^3P^e_1$	Mag. Dipole	6364 Å	
$^3P^e_1 \rightarrow {}^3P^e_2$	Mag. Dipole	63 µm	
$^3P^e_0 \rightarrow {}^3P^e_1$	Mag. Dipole	146 µm	

$$n\text{p}^5$$

We finally come to the np^5 ions, which have one hole. This makes the energy level structure similar to np^1, but once again with the fine structure levels reversed:

$$^2P^o_{3/2} < {}^2P^o_{1/2}.$$

The transition wavelength in Ne II is 12.8 µm.