Semi-forbidden, forbidden transitions and really forbidden (two-photon) transitions

S. R. Kulkarni

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In atomic spectroscopy, the most forbidden transition is $J = 0 \leftrightarrow J' = 0$. This stringent requirement comes from the fact that the emitted photon has an angular momentum of $\hbar$ which has to be supplied by the emitter. A species (atom or ion) excited to a $J' = 0$ can only decay to a $J = 0$ state either by collisional de-excitation or via the emission of *two* photons of opposite angular momentum and whose energies add up to the transition energy. The transition He $1s^2\ {}^1S_0$ to $1s2s\ {}^1S_0$ is the exemplar of two photon emission. A less well known example is C III $1s^22s^2\,{}^1S_0 \rightarrow 1s^22s2p\,{}^3P^o_0\,\lambda1909.6$. H $2s\,{}^2S_{1/2}$ can decays via two-photon continuum as well as magnetic dipole (M1). It simply happens to be the case that the latter dominates over the former.

The two-photon A-coefficients for He and H are similar to those of semi-forbidden lines. However, the two-photon A-coefficient for the aforementioned C III transition (which is a semi-forbidden line, in addition) is one of the smallest A-coefficients. Transitions with very low values of A-coefficients are highly valued by the atomic clock community (e.g., Sr optical clocks rely on ${}^1S_0$ to ${}^3P_0$ transition).

Finally, the total angular momentum is not J but $J + I$ where I is the nuclear spin. As a result, for nuclei with $I \neq 0$, $J = 0$ to $J' = 0$ decay with emission of a single photon becomes possible – the so-called "HPF" lines. As a result, HPF phenomenon makes it possible *to probe isotopic ratios in the interstellar medium using UV lines at modest spectral resolution – a novel diagnostic for the UVEX mission.*

Separately, as a result of investigations undertaken during this project I came to learn of the conditions under which lines are entered into the Atomic Spectra Database (ASD)/NIST. *Be aware: the absence of lines in ASD does not mean the lines do not exist. The default line list pertains to the natural mix of all stable isotopes of an element. Caution should be exercised when looking for lines with high precision in wavelength.*

Motivation. For the final (oral) exam for the graduate Ay 121 (Rybicki & Lightman) course I wanted to include a question or two on classifications of transitions. To this end I started off by reviewing the elegant Grotrian diagrams provided in the classic *Physics of the Interstellar and Intergalactic Medium* book (Draine 2011). ASD/NIST provides all the details (states, levels, A-coefficients and the type of perturber)[1].

Background: Under L-S coupling, allowed transitions (electric dipole, E1) must satisfy the selection rules listed below. The list is in decreasing order of importance.

1a. $\Delta J = 0, \pm 1$. **1b**. $J = 0 \not\leftrightarrow J' = 0$.
Rules 1a and 1b ("triangle rule") are usually explained by saying that the emitted photon has to carry off one unit of angular momentum. For instance, $J = 1$ to $J' = 1$ transition can be represented by an equilateral triangle whereas $J = 1$ to $J' = 0$ collapses to triangle with no width. **Violation of rule 1b is the primary focus of this write up.**

2. Parity must change (for a single electron: Δn any, $\Delta l = \pm 1$).

3. $\Delta L = 0, \pm 1$ (but $L = 0 \not\leftrightarrow L' = 0$).

4. $\Delta S = 0$
Transitions which violate this rule are classified as "semi-forbidden". Other names are inter-system (as in transitions between levels in two different spin families) or inter-combination ("IC"). This rule follows from the fact that spin wave-functions do not interact with the electric dipole. As a result, dipole transitions are expected to be in the same multiplicity family (e.g., singlets to singlets, triplets to triplets, as in helium). However, because of the deep connection between spin and magnetic moment, magnetic perturbations allow inter-combination transitions.

A violation of one or more of rules (1) to (3) are classified as "forbidden". Such transitions can proceed under one of the following frameworks: electric quadrupole (E2), magnetic dipole (M1) or magnetic quadrupole (M2). The ordering of A-coefficients is (i) Allowed ($10^8\,\mathrm{s}^{-1}$), (ii) Semi-forbidden ($10^2\,\mathrm{s}^{-1}$ with significant variation) and (iii) Forbidden (as low as $10^{-6}\,\mathrm{s}^{-1}$).

Organization of the report. Astronomers are introduced to two-photon emission in two different contexts. First, is the $J = 0 \rightarrow J' = 0$ transitions. He 1s2s $^1\mathrm{S}_0 \rightarrow$ 1s^2 $^1\mathrm{S}_0$ and is reviewed in §1. A related phenomenon is "HPF" lines which is discussed in §2. This section ends with astrophysical use of HPF lines. The second example of two-photon decay is the famous H 2s $^2\mathrm{S}_{1/2} \rightarrow$ 1s $^2\mathrm{S}_{1/2}$ two-photon continuum and is reviewed in §3. The report concludes with a summary of criteria for entry of lines in ASD and caveats on using ASD for isotopes (§4). The HPF channel was first recognized by Ira Bowen who, incidentally, served as the first Director of the Palomar Observatory and is in my inner

[1] This inquiry led me to a new phenomenon – whence this "report to self".

sanctum sanctorum (Zwicky, Hale, Bolton, Nelson and just a few others) The history of the recognition of HPF lines is summarized in §A.

1 $J = 0$ to $J' = 0$ transitions

The best known example of a $J = 0 \to J' = 0$ transition is the decay of He 1s2s $^1S_0$, the first excited state of helium on the singlet side, to the ground state, $1s^2\ ^1S_0$ (see §14.3 of Draine's book). The excited state can only[2] decay via two-photon emission or by collisional de-excitation. The A-coefficient for this line is not small, $50.9\,s^{-1}$ (Drake 1986).

For the oral exam I perused Grotrian diagrams in Appendix E of Draine's ISM book to look for other examples of $J = 0 \to J' = 0$ transitions. The first example I found were transitions between C III $1s^2 2s^2\ ^1S_0$ term and $1s^2 2s2p\ ^3P_{0,1,2}$ term (and summarized in Figure 1).

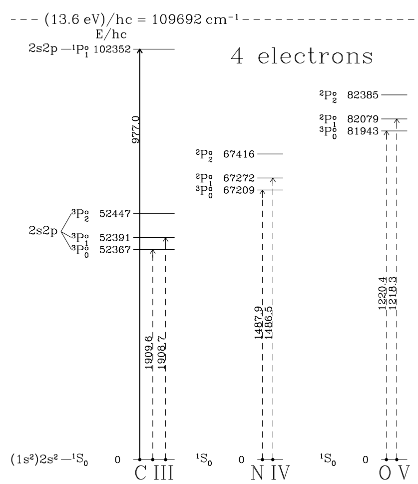

Figure 1: Figure from my electronic copy of Draine (2011) book. The 1908.7 Å is missing and the 1908.7 Å only arises in ^{13}C but not in ^{12}C.

1. C III] λ1908.7 $^1S_0 \to\ ^3P^o_1$. This is a semi-forbidden transition since the only violation is $\Delta S \neq 0$ ($A = 1.1 \times 10^2\,s^{-1}$; IC).
2. [C III] λ1906.7 $^1S_0 \to\ ^3P^o_2$. This is a forbidden transition because $\Delta J = 2$ ($A = 5.2 \times 10^{-3}\,s^{-1}$; M2). However, it was not listed in the figure.

[2] The only decay channel is via two photons as can be gathered by the absence of any entry for He I λ601 in ASD/NIST.

3. [C III] λ1909.6 ${}^1\mathrm{S}_0 \rightarrow\ {}^3\mathrm{P}^{\mathrm{o}}_0$. Given $J = 0 \rightarrow J' = 0$ this is strictly forbidden. Nonetheless, it was listed in the figure. Puzzled, I communicated with Draine who immediately realized that it was an error. This began a discussion that lasted over two days and the result is this report.

During the discussions Draine pointed out that interaction between $\boldsymbol{J}$ with nuclear spin $\boldsymbol{I}$ becomes possible, provided the magnitude of the nuclear spin, I $\neq 0$. In this case, the total angular momentum $\boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}$ is conserved. There is no longer a requirement to conserve J. Due to magnetic interaction the wave functions for $J = 0$ level can be written as linear combinations of various wave-functions over the range of values for F. As a result of this mixing channels for single photon emission channel for $J = 0$ to $J' = 0$ is opened up (see, for example, Brage et al. 1998 and references therein). These lines are called as HPF (for lines aided by hyperfine phenomenon) by some authors or "HF" by others.

2 Hyperfine induced lines (HPF)

The stable isotopes of carbon are ^{12}C (I = 0; terrestrial abundance of 99%) and ^{13}C (I = 1/2; 1%). ^{14}C (I = 0) has a lifetime of 5.7×10^3 yr. Thus, the abundant ^{12}C nor ^{14}C cannot exhibit HPF while ^{13}C can. Brage et al. (1998) present model estimate of the A-coefficient for ^{13}C HPF ($A = 9 \times 10^{-4}\,\mathrm{s}^{-1}$).

N IV and O V are isoelectronic with C III. The two lines (inter-combination and forbidden M2) corresponding to the C III lines discussed are N IV] λ1486 ($A = 5.9 \times 10^2\,\mathrm{s}^{-1}$, [N IV] λ1483 ($A = 1.1 \times 10^{-2}\,\mathrm{s}^{-1}$), The stable isotopes of nitrogen are ^{14}N (I = 1; 99.5%) and ^{13}N (I = 1/2; 0.5%). From Draine I learnt that HPF [N IV] λ1487.9 ${}^1\mathrm{S}_0 \rightarrow\ {}^3\mathrm{P}^{\mathrm{o}}_0$ ($A = 4 \times 10^{-4}\,\mathrm{s}^{-1}$) was detected in the planetary nebula NGC 3918 (Brage et al. 2002). The A-coefficient inferred from these observations agrees with that computed from theory, $A \approx 4 \times 10^{-4}\,\mathrm{s}^{-1}$ (Brage et al. 1998).

The inter-combination and forbidden lines of O V are O V] λ1214 ($A = 2.3 \times 10^3\,\mathrm{s}^{-1}$) and [O V] λ1218 ($A = 2.1 \times 10^{-2}\,\mathrm{s}^{-1}$). The stable isotopes of oxygen are ^{16}O (I = 0; 99.7%), ^{17}O (I = 5/2; 0.4 ppt) and ^{18}O (I = 0; 2.2 ppt). Brage et al. (1998) present model estimates of the A-coefficient of ^{17}O HPF ($A = 4 \times 10^{-4}\,\mathrm{s}^{-1}$). For further details of HPF lines of the Be iso-electronic sequence please see Brage et al. (1998) and Laughlin (1980).

Following this discussion Draine revised the Grotrian diagrams for the C III iso-electronic sequence. The revised figure (Figure 2) now includes the HPF lines from ^{13}C, ^{14}N and ^{15}O. Draine informed that the revised figure will be incorporated in the next edition of the ISM book.

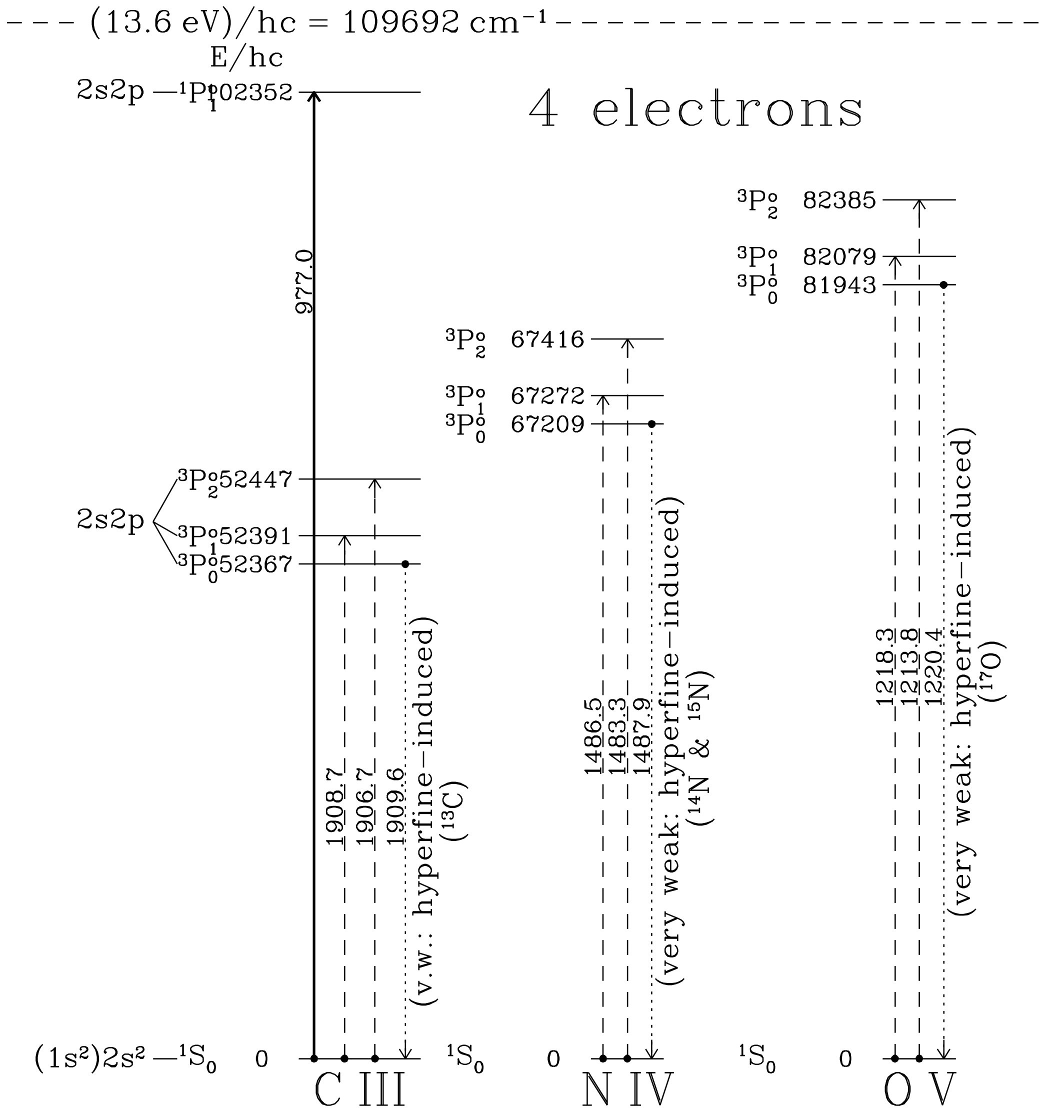

Figure 2: The revised Grotrian diagram of Be-like ions (provided by Draine). The HPF lines have been added. This figure will appear in the next edition of Draine's ISM book.

2.1 Mg I, Al II and Si III

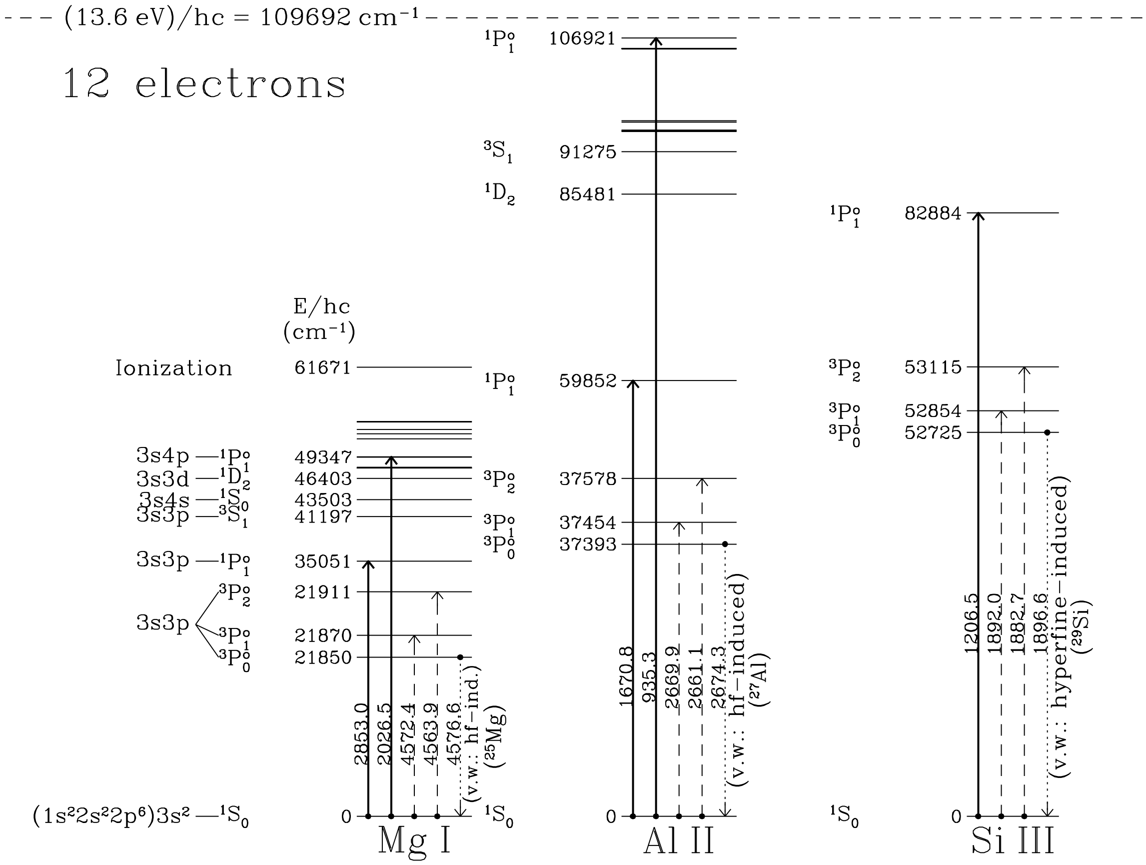

Figure 3: The revised Grotrian diagram of Mg I, Al II and Si III which will appear in the next edition of Draine's ISM book.

The discussion in the previous subsection also applies to the iso-electronic sequence [Ne] $3s^2$: Mg I, Al II and Si III. From ASD/NIST I found the A-coefficients for M2 ($^3P^o_2 \rightarrow {}^1S_0$) and IC ($^3P^o_1 \rightarrow {}^1S_0$) lines as follows: [Mg I] $\lambda 4564$ ($A = 3.9{\times}10^{-3}\,s^{-1}$) & Mg I] $\lambda 4572$ ($A = 2.5 \times 10^2\,s^{-1}$); and [Al II] $\lambda 2661$ ($A = 3.3 \times 10^{-3}\,s^{-1}$) & Al II] $\lambda 2669$ ($A = 3.28 \times 10^3\,s^{-1}$). **Strangely enough, [Si III]** λ**1882.7 and Si III]** λ1892.0 **are not listed in ASD**; see §4 for an explanation. The revised Grotrian diagram can be found in Figure 3.

2.2 [Al II] λ 2674.3 HPF

Terrestrial aluminum consists only[3] of ^{27}Al (I = 5/2). However, ASD/NIST has no entry for the expected HPF line, [Al II] λ2674.3 $^1S_0 \rightarrow {}^3P^o_0$. As can be gathered from Rosenband et al. (2007) the ^{27}Al HPF line is an important line in the clock community: "The $^1S_0 \rightarrow {}^3P_0$ transition in Al^+ has long been recognized as a good clock transition [1, 2], due to its narrow natural line-width (8 mHz), and its insensitivity to magnetic fields and electric field gradients (J = 0), which are common in ion traps. More recently, this transition was also found to have a small room-temperature blackbody radiation shift. However, difficulties with direct laser cooling and state detection have so far prevented its use."

The ^{27}Al FPS line frequency has been measured to a few Hz, 1 121 015 393 207 851(8) Hz and the exponential lifetime is $\tau = 20.6 \pm 1.4\,\mathrm{s}$ (Rosenband et al. 2007). From the latter I deduce $A = 1/\tau \approx 5 \times 10^{-2}\,\mathrm{s}^{-1}$

2.3 [Mg I] λ 4476.6 HPF

The stable isotopes of magnesium are ^{24}Mg (I = 0), ^{25}Mg (I = 5/2) and ^{26}Mg (I = 0) and their terrestrial abundances are 79%, 10% and 11%, respectively. Thus only ^{25}Mg should exhibit HPF.

Curiously NIST has an entry for [Mg I] λ4576.6 $^3P^o_0 \rightarrow {}^1S_0$. Intrigued I communicated my puzzlement to ASD. The reply from Dr. Kramida is as follows "*Thank you for pointing out the error in ASD: the 3s2 1S0-3s3p 3P0 transition in Mg I is erroneously given therein as an allowed (E1) transition. I am sorry I did not catch it at first sight. Now I looked at it more closely and I see that this value was not given in the compilation of Kelleher and Podobedova (2008) from which the rest of A-values are given for Mg I. I do not have any trace of this dataset on my computer. Somebody else must have entered it and made a mistake. The oscillator strength and line strength values appear to have been recalculated from the A-value assuming that it is an E1 transition, which is completely wrong. The reference to the opacity database (Butler et al. 1993) is also incorrect. I do not know where the listed A-value comes from. So, in the next release of ASD, I am going to delete this A-value along with the reference to its source and specify the transition type as "HF" (hyperfine-induced). As we discussed, it is not possible to specify an A-value of such transition for a natural mixture of isotopes. But the transition energy or wavelength is nonetheless legitimate.*

[3]because all isotopes are unstable on timescales of milliseconds to seconds, except for ^{26}Al which decays on a timescale of a million years

2.4 [Si III] λ 1896.6 HPF

The stable isotopes of silicon are ^{28}Si (I = 0), ^{29}Si (I = 1/2) and ^{30}Si (I = 0) and their terrestrial abundances are 92%, 5% and 3%, respectively. As with all other HPF lines, ASD/NIST has no entry for Si III HPF.

2.5 Use of HPF in probing isotopic ratios

Brage et al. (1998) point out that ^{12}C has no nuclear spin but I = 1/2 for ^{13}C. As a result, $^{13}C^{++}$ will exhibit HFS while $^{12}C^{++}$ will not. Thus observations of planetary nebulae can potentially yield ^{13}C/^{12}C.

^{26}Al (I = 5) with a half-lifetime of about a million years is a tracer of nucleosynthesis on mega year timescales. As such, there is interest in tracing this species in the Galactic ISM. Unfortunately, a high spectral resolution is needed to distinguish HPF ^{26}Al from HPF ^{27}Al.

Note to self: Brage et al. (1998) and Brage et al. (2002) are thorough papers with exquisite details. Useful for setting problem set.

3 The hydrogen two-photon transition

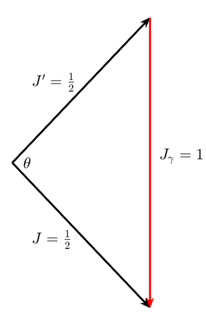

Figure 4: The angular momentum of the H atom before emission ($J = 1/2$) and after emission ($J' = 1/2$) is shown in black. The length of each vector is $\sqrt{J(J+1)} = \sqrt{3}/2$. The angle θ is given by $\cos(\theta) = -1/3$. The red vector is the angular momentum of the emitted photon, $J_\gamma = 1$. As such it has a length of $\sqrt{2}$.

Consider the H 2s $S_{1/2} \rightarrow$ 1s $S_{1/2}$ transition. As can be seen from Figure 4 this transition does satisfy the triangle rule: $\Delta J = 0, \pm 1$ and $J = 0 \nrightarrow J' = 0$. This transition is forbidden because it fails the parity requirement. However, M1 transitions do not demand parity inversion. Indeed, a perusal of NIST shows that 2s $S_{1/2} \rightarrow$ 1s $S_{1/2}$ can take place[4] via M1. The A-coefficient is small, $2.5 \times 10^{-6}\,\mathrm{s}^{-1}$.

Apparently for hydrogen, as evidence by a large two-photon A-coefficient, $8.2\,\mathrm{s}^{-1}$ (Drake 1986), second-order interactions between the atom and the electromagnetic field dominates over M1. The resulting two-photon emission is the second most luminous "feature"[5] after Lyα. Useful references: Drake (1986; A-coefficient), Chluba & Sunyaev (2008; extensive discussion in the context of the early Universe) and Kulkarni (2022; two-photon contribution to a variety of phenomena – earth's exosphere, solar system inter-planetary medium, Galactic ISM, strong shocks). Incidentally, it appears that the two-photon process also operates for nd $\rightarrow$ 1s transitions (see Chluba & Sunyaev 2008).

4 Atomic Spectra Database/NIST

In this section, I summarize what I learnt from my communications with ASD/NIST, specifically Dr. Alexander Kramida. First, I learnt that the default input choice (e.g. C I) shows the spectrum (and constructed energy levels) of the *mix of terrestrial isotopes*. If you want a specific isotope then you need to specify, for example, 12C I or 13C II. Note that the isotope part of the database is relatively sparse.

The Rydberg for an atom consisting of an electron (m_e) and a nucleus (M) is $R = (\mu/m_e)R_\infty$ where $\mu = Mm_e/(M + m_e)$ is the reduced mass and R_∞ is the Rydberg constant ($109,737.3\,\mathrm{cm}^{-1}$). The scaling factor is $f = \mu/m_e$. The difference in this scaling factor of two isotopes (mass, M and $M + m_n$; here, m_n is the mass of a neutron) is $\Delta f \approx (m_n/M)(m_e/M)$. For ^{12}C and ^{13}C, $\Delta f = 3.8 \times 10^{-6}$ (corresponding to $1\,\mathrm{km\,s^{-1}}$) which is small enough that none but the highest resolution spectroscopist will be concerned with.

Second, I found that ASD will only allow entry of data for lines which have sufficient data (in particular, precision of wavelength, precision of A-coefficients). Dr. Kramida explained that the A-coefficients of the two transitions resulting from S III $^1S_0$-$^3P_{0,1,2}$ were not known with sufficient precision to warrant their entry into the ASD data. The mystery of missing lines of S III (§2.1) is solved!

Finally, the absence of HPF lines is now understandable. They could be missing due to several reasons: (1) arising in a a rare isotope (e.g., ^{13}C) or (2) lacking atomic data with sufficient precision.

Acknowledgements. I thank Professor Draine for discussions and Dr. Alexander Kramida

[4]it is a small effect made only possible by relativistic corrections to the magnetic dipole.

[5]Very few astronomers are aware of this fact.

of ASD/NIST for promptly and patiently answering basic questions from me.

References

Brage, T., Judge, P. G., et al., Hyperfine Induced Transitions as Diagnostics of Isotopic Composition and Densities of Low-Density Plasmas, The Astrophysical Journal, 500, 507 (1998)

Brage, T., Judge, P. G., Proffitt, C. R., Determination of Hyperfine-Induced Transition Rates from Observations of a Planetary Nebula, Physical Review Letters, 89, 281101 (2002)

Chluba, J., Sunyaev, R. A., Induced two-photon decay of the 2s level and the rate of cosmological hydrogen recombination, Astronomy and Astrophysics, 446, 39 (2006)

Curtis, L. J., Atomic Structure and Lifetimes, Atomic Structure and Lifetimes, 282 (2003)

Draine, B. T., Physics of the Interstellar and Intergalactic Medium, Princeton University Press (2011)

Drake, G. W. F., Spontaneous two-photon decay rates in hydrogen-like and helium-like ions, Physical Review A, 34, 2871 (1986)

Huff, L. D. and Houston, W. V., The Appearance of "Forbidden Lines" in Spectra, Physical Review, 36, 842 (1930)

Kulkarni, S. R., The Far Ultra-violet Background, Publications of the Astronomical Society of the Pacific, 134, 084302 (2022)

Laughlin, C., Radiative decay of the 2 $^3P^0_0$ level of beryllium-like ions, Physics Letters A, 75, 199 (1980)

Rosenband, T., Schmidt, P. O., et al., Observation of the S01P03 Clock Transition in Al+27, Physical Review Letters, 98, 220801 (2007)

A History of HPF

L. Curtis (2003) in his book *Atomic Structure and Lifetimes* states "The phenomenon was first discussed in Huff & Houston (1930)[6] by Bowen, who pointed out that the substantial

[6] In 1930, Huff & Houston (both at Caltech) were investigating [Hg] λ2270 which results from $[Xe]4f^4 5d^{10} 6s^2\ ^1S_0 \rightarrow [Xe]f4^4 5d^{10} 6s6p\ ^3P_2$. They attributed this to octopole radiation. In a note added at the end of the paper the authors state "*Dr. Bowen has called our attention to the fact that the line λ 2270 in Hg is probably due to the coupling of the nuclear spin with the electronic angular momentum. An estimate based on the relative separation of the multiplets and the hyperfine structure gives the right order*

strength that was observed in the $6s^2\ ^1S_0 \to 6s6p\ ^3P_2$ in the spectrum of Hg I was primarily due to E1 radiation caused by coupling with nuclear spin ...Bowen's conclusion was confirmed by Mrozowski (1938), who experimentally observed the $6s^2\ ^1S_0 \to 6s6p\ ^3P_0$ line at 2656 Å in Hg I. This transition would be rigorously forbidden to all multiple orders of single-photon decay in an atom with a spin-less nucleus by the $J = 0 \nrightarrow J' = 0$ requirement. Mrozowski attributed the appearance of this line to coupling between the magnetic moments (spin and orbital) of the electron and the spin of the nucleus." The A-coefficient of $^1S_0 \to^3 P_0$ rapidly increases with Z, reaching to values comparable to E1 transitions (see Figure 11.2 in Curtis 2003).

B Physics of Two-photon emission

The discussion is from Rybicki & Lightman (Chapter 10). The relativistic generalization of a valence electron orbiting a nucleus is given by

$$H = [(c\boldsymbol{p} - e\boldsymbol{A})^2 + m^2c^4]^{1/2} + e\phi$$

where the electromagnetic field is specified by the electric scalar potential, ϕ and the magnetic vector potential, $\boldsymbol{A}$. Using the Coulomb gage, $\nabla \cdot \boldsymbol{A} = 0$ that $\boldsymbol{p}$ and $\boldsymbol{A}$ commute. A series of approximations are made. First, the non-relativistic approximation results in

$$H = \left[\frac{p^2}{2m} + e\phi\right] - \frac{e}{mc}\boldsymbol{A}\cdot\boldsymbol{p} + \frac{e^2A^2}{2mc^2}$$

The perturbation terms are the last two terms on the RHS. The $\boldsymbol{A}\cdot\boldsymbol{p}$ term is responsible for one-photon emission. Expansion of $A \propto \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ results in E1, M1, E2, M2 and so on outcomes. Two-photon emission results from the A^2 term.

The ratio of the two perturbing terms is

$$\eta = \frac{epA/mc}{e^2A^2/2mc^2} = \frac{2ev/c}{\alpha^2 a_0 A}\ .$$

Since, $v/c \approx \alpha$ and $A \approx \lambda E$ where E is the electric field and λ is the wavelength we have

$$\eta^2 \approx \frac{4\hbar\omega}{2\pi\alpha a_0^2 \lambda E^2}\ .$$

Since $\lambda \approx a_0/\alpha$ and $n_{\rm ph} \approx E^2/\hbar\omega$ we have $\eta^2 = (n_{\rm ph}a_0^3)^{-1} \gg 1$; here, $n_{\rm ph}$ is the number density of photons. One requires $n_{\rm ph}$ to exceed $10^{25}\,{\rm cm}^{-3}$ for two-photon emission to be comparable to the photon production by the first term.

of magnitude for the intensity. The statements made above with respect to J really refer strictly to the total angular momentum."

Two-photon emission can take place for $J = 0$ to $J' = 0$ transitions because two photons with opposite angular momentum can be emitted and thus there is no demand for any additional angular momentum from the atom.

This discussion shows why two-photon emission is expected to be weak but it does not explain why two-photon emission is strong for H 2s $\rightarrow$ 1s.

C Discussions with Prof. Jens Chluba

Dear Prof: Chluba: What I am puzzled is why there is such a larger variation in the A-coefficients of two-photon continuum? I do not have the necessary background in quantum mechanics to answer this and was hoping perhaps you may be able to resolve this puzzle for me – SRK.

This is an excellent and non-trivial question. For the HI 2s-1s there is no resonant lower-lying intermediate state (only virtual transitions to higher np-level and the continuum contribute), so the suppression relative to the 2p-1s dipole transition comes from A2s1s $\sim \alpha^8$ versus A2p1s $\sim \alpha^5$ primarily, being higher order in perturbation theory as your notes correctly say.

I assume you are now asking why the two-photon transition from higher levels (and similarly Raman-scattering events) have so much higher rates? This is because you have real resonant contributions for ns-1s and nd-1s transitions. It is in fact physically not easy to separate these resonant contributions which can be thought of as a sequence of two single photon transitions. These coherent contributions only matter in low density media, where collisions do not interfere with the atom on the timescale involved in the transition. In the lab, we never have this but in the early Universe we do, which is the reason one has to treat the line profile corrections and effects on the radiative transfer carefully. Because of these real resonant contributions to lower lying level, the two-photon rates are basically as large as the single dipole rates. For example the coherent 3s-1s two-photon transition has a net rate that is comparable to the 3s-2p transition rate for that reason.

SRK: The 3s-1s two-photon process. Is this 3s to 2p and then 2p to 1s? (two distinct and narrow lines). If so, does this process increase the A-coefficient of 3s-2p (to that computed assuming only A.p perturbation).

The coherent 3s-1s transition indeed has two resonance as you correctly guessed. The lifetime of the 3s state is slightly modified by this, but usually other effects are more important.

SRK: You stated "These coherent contributions only matter in low density media, where collisions do not interfere with the atom on the timescale involved in the transition. In the *lab, we never have this but in the early Universe we do, which is the reason one has to treat the line profile corrections and effects on the radiative transfer carefully."*

However, collisions merely suppress ($n/n_{\rm crit}$) radiation for that channel. So, is it not simply the case that the effect is easier to see at low density. See for example, J. Spyromilio (PASP, 2025).

I dont think it is as simple. All processes act at the same time and compete. We usually think of all of the processes as independent quantum acts with specified initial and final states (including some level of uncertainties for unstable states). Two photon transition can only occur in their coherent (unperturbed form) if we have no collision or radiative process destroying the coherence while the quantum act is happening. In the QM description, the transition between the regimes is not even built in properly and that is why we usually simply compare the branching ratios of the net rates etc. Einstein coefficients themselves are an approximation for the much more complicated (frequency-resolved) quantum process that plays a role in the two photon physics of recombination. With the standard textbook approximations one does not get full equilibrium far from the resonance and for recombination one has to go some ~ 100 to 10^4 Doppler widths out into the wings. One really has to look at the full differential process and mixing with collisional processes and other radiation processes to fully solve this. Very rich quantum physics, but still approximate.

SRK: Can you please explain why the A-coefficient for He 2s-1s (singlet) is so much higher than CIII transition that I discuss in my writeup?

I had a suspicion and just looked at the Laughlin paper that I think confirmed it. The considered transition is E1 + M1, so magnetic dipole involved. These are suppressed usually over electric dipole transitions. For HI and also HeI it is E1+E1 unless I am mistaken. But I must also admit that it has been a while since I have been doing these kind of calculations, so I may be wrong.

Hossein Sadeghpour (https://astronomy.fas.harvard.edu/people/hossein-sadeghpour) might have a quick and more satisfying answer though! We had several discussions about two-photon processes back in the days.

Dear Dr. Sadeghpour:

Whilst teaching Rybicki & Lightman for our grads I become curious of the A-coefficients for two-photon continuum. I got in touch with Dr. Chluba and he directed me to you.

Please permit me to provide the background. Let us consider three different two photon processes: (1) He 1s2s 1S to 1s2 1S, (2) H 2s to 1s and (3) [CIII] $1s^2 2s^2$ $1S_0$ to $1s^2 2s2p$ $^3{\rm P}_0$.

The A-coefficients for (1) and (2) are well known and given in textbooks. For (3) C. Laughlin (1980; Physics Letter A; 75, 199) provides A-coefficient ($5\times10^{-18} Z^9\,{\rm s}^{-1}$). I was *curious why is this so much smaller than for case (1) and case (2).*

Sadeghpour: Thank you for the note. I will look into it in more details, but at first glance, while for H and He, the transitions are dipole parity forbidden (hence two photons), the CIII transition is doubly forbidden (total spin S, single $\rightarrow$ triplet) and the more strict rule (total angular momentum J, $0 \rightarrow 0$).

The $^1S_0$ to $^3P_0$ transition is precisely the ultra narrow-band transition which is cycled in Sr optical clocks.