Atomic and Molecular Data Needs for Astrophysics

Robert L. Kurucz

Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, U.S.A.

Abstract. We need a list of all the energy levels of all atoms and molecules that matter (qualifiers below). Except for the simplest species, it is impossible to generate accurate energy levels or wavelengths theoretically. They must be measured in the laboratory. From the list of energy levels can be generated all the lines. Given the low accuracy required, 1 - 10%, all the other data we need can eventually be computed or measured. With the energy levels and line positions known, one can measure gf values, lifetimes, damping, or one can determine a theoretical or semiempirical Hamiltonian whose eigenvalues and eigenvectors produce a good match to the observed data, and that can then be used to generate additional radiative and collisional data for atoms or molecules.

For atoms and ions, we need all levels, including hyperfine and isotopic splittings, for n $\leq$ 9 below the lowest ionization limit and as much as practicable above. Lifetimes and damping constants depend on sums over the levels. Inside stars there are thermal and density cutoffs that limit the number of levels, but in circumstellar, interstellar, and intergalactic space, photoionization and recombination can populate high levels, even for high ions. We need all stages of ionization for elements at least up through Zn.

In the sun there are unidentified asymmetric triangular features that are unresolved multiplets of light elements with n $\leq$ 20. Simple spectra should be analyzed up to n = 20. Levels that connect to the ground or to low levels should be measured to high n, say n = 80. The high levels are necessary to match line series merging into continua.

All the magnetic dipole, electric quadrupole, and maybe higher-pole, forbidden lines are required as well. Most of the universe is low density plasma or gas. If the Hamiltonian is well determined, forbidden lines should be reliably computable.

For molecules, we need all levels below the first dissociation limit and as much as is practicable above, especially levels of all states that connect to the ground state. Stars populate levels to high V and to high J. In the sun there are many broad bumpy features that are molecular bands that are not in the line lists. For the cooler stars we need all the diatomics among all the abundant elements, and, essentially, the hydrides and oxides for all elements (especially ScO, TiO, VO, YO, ZrO, LaO). For M stars triatomics also become important. Much more laboratory and computational work is needed for H_2O. In the brown dwarfs and "planets" methane is important and it needs more laboratory and computational work.

We can produce more science by investing in laboratory spectroscopy rather than by building giant telescopes that collect masses of data that cannot be correctly interpreted.

INTRODUCTION

Astrophysicists work on “Important”, “Big” problems and they think that the basic physics that they require to solve their problems has already been done, or, if it has not been done, it is easy and can be readily produced, as opposed to the hard problems they are working on. They have it backward. Getting the basic data is the hard part. When all the basic physics is known, pushing the “state-of-the-art” becomes straightforward.

Half the lines in the solar spectrum are not identified. All the features are blended. Most features have unidentified components that make it difficult to treat any of the identified components in the blend. And even the known lines have hyperfine and isotopic splittings that have not yet been measured. Is an asymmetry produced by a splitting. or by a velocity field, or both? It is very difficult to determine abundances, or any property, reliably when you do not know what you are working with.

For planetary and telluric atmosphere projects the solar irradiance spectrum is required as the input at the top of the atmosphere. It has never been observed. People ask me to compute it. I can compute it theoretically using both known and predicted lines and get agreement averaged over a nanometer but there is no way to predict the resolved spectrum when only half the lines are known. In other stars the situation is worse because the signal-to-noise and resolution of the observations are worse. Logically one has to know a priori what is in the spectrum in order to interpret it; there is not enough information in the observed spectrum itself.

Basically we need a list of all the energy levels of all atoms and molecules that matter (qualifiers below). From that list can be generated all the lines. With the energy levels and line positions known, one can measure gf values, lifetimes, damping, or one can determine a theoretical or semiempirical Hamiltonian whose eigenvalues and eigenvectors produce a good match to the observed data, and that can then be used to generate additional radiative and collisional data for atoms or molecules.

For atoms and ions, we need all levels, including hyperfine and isotopic splittings, for n $\leq$ 9 below the lowest ionization limit and as much as practicable above. Th is the only element that does not have splitting. Lifetimes and damping constants depend on sums over the levels. Inside stars there are thermal and density cutoffs that limit the number of levels, but in circumstellar, interstellar, and intergalactic space, photoionization and recombination can populate high levels, even for high ions.

One very important problem is diffusion of heavy elements inside stars because it changes the density and reaction rates. The radiative acceleration is computed by integrating over the line spectrum. At the surface some elements can be enhanced by a factor of 10^4. If the diffusion is deep inside the star, spectra for high stages of ionization are required.

In the sun I see unidentified asymmetric triangular features that are unresolved multiplets of light elements with n $\leq$ 20. Simple spectra should be analyzed up to n = 20. Levels that connect to the ground or to low levels should be measured to high n, say n = 80. The high levels are necessary to match line series merging into continua.

All the magnetic dipole, electric quadrupole, and maybe higher-pole, forbidden lines are required as well. Most of the universe is low density plasma or gas. If the Hamiltonian is well determined, forbidden lines should be reliably computable.

For molecules, we need all levels below the first dissociation limit and as much as is practicable above, especially levels of all states that connect to the ground state. Except for H_2(BX,CX), far ultraviolet bands have been ignored unless they appear as interstellar lines. We see H_2 lines in stars as hot as 8000K when the stars have low metal abundances so that the lines are not masked.

In the sun we see, and have linelists for, C_2(AX,ba,da,ea), CN(AX,BX), CO(AX,XX), H_2(BX,CX), CH(AX,BX,CX), NH(AX,ca), OH(AX,XX), MgH(AX,BX), SiH(AX), SIO(AX,EX,XX). The isotopomers are included. Some stellar spectroscopists have more recent linelists than I do. Mine are based on old laboratory data and were computed with rotationless RKR potentials. They all have to be brought up to date, or even further improved, and expanded to higher V and J levels. In many cases there are new analyses based on FTS spectra. Ions and a few minor molecules have to be added to the linelist as well. In the sun there are many broad bumpy unidentified features that are molecular bands that are not in the line lists. Most of them are probably just high-V transitions. It is important that the laboratory analyses include all the isotopomers. They are needed to interpret the stellar spectra. When they are not measured in the laboratory we have to make up our own predicted linelists for them.

For the cooler stars we need all the diatomics among all the abundant elements, and, essentially, the hydrides and oxides for all elements (such as ScO. TiO, VO, YO, ZrO, LaO, etc.). Ca appears as CaOH and CaH, not CaO. I use the TiO linelist from Schwenke (1998) [1] with 38 million lines.

Stars that are evolved and have high C abundances from nuclear burning can bind all the O into CO so that there are no other oxides, just C-bearing molecules. CN and C_2 bands are everywhere.

For M stars cooler than 3500K triatomics also become important. Much more laboratory and computational work is needed for H_2O. I currently use the linelist from Partridge and Schwenke (1997) [2] with 66 million lines.

In the brown dwarfs and “planets” methane is important and it needs more laboratory and computational work. This is too cool and too hard for me.

58, 154, 500 MILLION LINES

Here is the background starting with my calculations at the San Diego Supercomputer Center in the 1980s. I have computed line data for 42 million lines of the iron group elements [3] plus I have all the data from the literature for all elements. I have computed line data for 16 million diatomic molecular lines (Some as much as 20 years ago.) I have tabulated opacities for more than 30 abundances, for temperatures from 2000K to 200000K using all 58 million lines at 3.5 million wavelengths from 10 nm to 10000 nm. I have computed more than 9000 models for a wide range of abundances for 3500K to 50000K effective temperature. I have computed a solar model that matches the observed energy distribution. I have computed fluxes and colors for the models. I have distributed all of this as it was produced, to supernova modelers, to galaxy modelers, to interior modelers, to stellar atmosphere modelers, to photometrists, etc. My line data are used as input to modelling codes for atmospheres, novas, and supernovas that are completely independent of my codes. They are basic data. Only 1 per cent (i.e., 600,000) of my computed lines have accurate wavelengths between known levels because the laboratory analyses have not yet found the levels and need improvement. When published theory or laboratory f values or broadening data seem better than mine, I use the better data. This "good" line list is the input for spectrum synthesis programs. I put the programs and data on CD-ROMs and I have distributed 26 titles so far. They are now on my web site.

I have added the TiO and H_2O line lists from Schwenke and I have thrown out my old TiO linelist. That leaves me with 154 million lines with which I can compute reasonable models for M stars down to 3500K.

To compute the iron group line lists I made Slater-expansion model Hamiltonians that included as many configurations as I could fit into the Cray. I used Hartree-Fock Slater integrals (scaled) for starting guesses and for higher configurations that had no laboratory energy levels. All configuration interactions were included. I then determined the Slater integrals for the observed configurations by least squares fitting the eigenvalues computed from the Hamiltonian matrix to the observed energies. The complication was that the eigenvalues and the observed energies had to be correlated by hand each iteration and more than a hundred interations were often required for convergence. My computer programs for these procedures have evolved from Cowan's (1968) programs [4]. Transition integrals were computed with scaled-Thomas-Fermi-Dirac wavefunctions and the whole transition array was produced for each ion. Radiative, Stark, and van der Waals damping constants and Landé g values were automatically produced for each line. The first nine ions of Ca through Ni produced 42 million lines. Eigenvalues were replaced by measured energies so that lines connecting measured levels have correct wavelengths. Most of the lines have uncertain wavelengths because they connect predicted rather than measured levels.

I am now computing or recomputing all the atoms and diatomic molecules. My old Cray programs from the 1980s were limited to 1100 x 1100 arrays in the Hamiltonian for each J. With my Alpha workstation I can easily run cases with 3000 x 3000 arrays so that I can include many more configurations and many more configuration interactions. The larger arrays produce about 3 times as many lines. At present I am limited to 61 even and 61 odd configurations and I try to include everything up through n = 9. I decided to test the new program on Fe I and Fe II to see whether there was any great difference in the low configurations compared to those from the Cray program. The major result was that the electric quadrupole transitions were 10 times stronger than before because the transition integrals are weighted by r^2 —they become very large for high n, and because there are numerous configuration interactions that mix the low and high configurations. As a check I was able to reproduce Garstang's (1962) lower results [5] by running his three configurations with my program. Since my model atom is still only a subset of a real Fe II ion, the true quadrupole A values are probably larger than mine. The magnetic dipole lines are affected by the mixing but the overall scale does not change.

EXAMPLES

Here I show sample statistics from my new semiempirical calculations for Fe II, Ni I, and Co I to illustrate how important it is to do the basic physics well and how much data there are to deal with. Ni, Co, and Fe are prominent in supernovas, including both radioactive and stable isotopes. There is not space here for the lifetime and gf comparisons. Generally, low configurations that have been well studied in the laboratory produce good lifetimes and gf values while higher configurations that are poorly observed and are strongly mixed are not well constrained in the least squares fit and necessarily produce poorer results and large scatter. My hope is that the predicted energy levels can help the laboratory spectroscopists to identify more levels and further constrain the least squares fits. From my side, I check the computed gf values in spectrum calculations by comparing to observed spectra. I adjust the gf values so that the spectra match. Then I search for patterns in the adjustments that suggest corrections in the least squares fits.

As the new calculations accumulate I will put on my web site the output files of the least-squares fits to the energy levels, energy level tables, with E, J, identification, strongest eigenvector components, lifetime, A sum, C_4, C_6, Landé g. The sums are complete up to the first (n = 10) energy level not included. There will be electric dipole, magnetic dipole, and electric quadrupole line lists. Radiative, Stark, and van der Waals damping constants and Landé g values are automatically produced for each line. Hyperfine and isotopic splitting are included when the data exist but not automatically. Eigenvalues are replaced by measured energies so that lines connecting measured levels have correct wavelengths. Most of the lines have uncertain wavelengths because they connect predicted rather than measured levels. Laboratory measurements of gf values and lifetimes will be included.

When computations with the necessary information are available from other workers, I am happy to use those data instead of repeating the work.

Fe II

Based on Johansson (1978) [6] and on more recent published and unpublished data. Johansson has data for more than 100 energy levels that I do not yet have.

		d^7						
$d^6$4s	$d^5$4s^2	$d^6$4d	$d^5$4s4d			$d^4$4s^{2}4d	$d^5$4p^2	
$d^6$5s	$d^5$4s5s	$d^6$5d	$d^5$4s5d	$d^6$5g	$d^5$4s5g	$d^4$4s^{2}5s		
$d^6$6s	$d^5$4s6s	$d^6$6d	$d^5$4s6d	$d^6$6g	$d^5$4s6g			
$d^6$7s	$d^5$4s7s	$d^6$7d	$d^5$4s7d	$d^6$7g	$d^5$4s7g	$d^6$7i	$d^5$4s7i	
$d^6$8s	$d^5$4s8s	$d^6$8d	$d^5$4s8d	$d^6$8g	$d^5$4s8g	$d^6$8i	$d^5$4s8i	$d^5$4s9l
$d^6$9s	$d^5$4s9s	$d^6$9d	$d^5$4s9d	$d^6$9g	$d^5$4s9g	$d^6$9i	$d^5$4s9i	$d^6$9l

$d^6 4p$	$d^5 4s4p$	$d^6 4f$	$d^5 4s4f$			$d^4 4s^2 4p$	$d^4 4s^2 4f$
$d^6 5p$	$d^5 4s5p$	$d^6 5f$	$d^5 4s5f$			$d^4 4s^2 5p$	
$d^6 6p$	$d^5 4s6p$	$d^6 6f$	$d^5 4s6f$	$d^6 6h$	$d^5 4s6h$		
$d^6 7p$	$d^5 4s7p$	$d^6 7f$	$d^5 4s7f$	$d^6 7h$	$d^5 4s7h$		
$d^6 8p$	$d^5 4s8p$	$d^6 8f$	$d^5 4s8f$	$d^6 8h$	$d^5 4s8h$	$d^6 8k$	$d^5 4s8k$
$d^6 9p$	$d^5 4s9p$	$d^6 9f$	$d^5 4s9f$	$d^6 9h$	$d^5 4s9h$	$d^6 9k$	$d^5 4s9k$

configurations	46 even	39 odd
levels	19771 even	19652 odd
largest J matrix	2965 even	3007 odd
known levels	403 even	492 odd
metastable levels	72 even	1 odd

[The odd metastable level $(^2I)4sp(^3P)\ ^4K_{8.5}$ is predicted at 103122 ± 150 cm^{-1}.]

Hamiltonian parameters	2645 even	2996 odd
free LS parameters	58 even	51 odd
standard deviation	56 cm^{-1} even	75 cm^{-1} odd
total E1 lines saved	7719063	old K88 [3] 1264969
between known levels	81225	old K88 45815
total M1 lines saved	1852641 even	2468074 odd
between known levels	28102 even	41374 odd
between metastable	1180 even	0 odd
total E2 lines saved	10347332 even	13179033 odd
between known levels	49019 even	71225 odd
between metastable	1704 even	0 odd

[My intuition tells me to keep all the forbidden lines, not just the ones connecting metastable levels. I do not have time to think about it now, but since the quadrupole A values get larger as n gets larger and since there are more than 10 million lines, they must somehow make our lives more complicated.]

isotopic components	^{54}Fe	^{55}Fe	^{56}Fe	^{57}Fe	^{58}Fe	^{59}Fe	^{60}Fe
fractional abundances	.059	.0	.9172	.021	.0028	.0	.0

There are 4 stable isotopes. ^{57}Fe has not yet been measured because it has hyperfine splitting. Rosberg, Litzén, and Johansson (1993) [7] have measured ^{56}Fe–^{54}Fe in 9 lines and ^{58}Fe–^{56}Fe in one line. I split the computed lines by hand.

Ni I

Ni I mostly based on Litzén, Brault, and Thorne (1993) [8] with **isotopic splitting**.

configurations	46 even	48 odd
levels	3203 even	4800 odd
largest J matrix	517 even	840 odd
known levels	130 even	153 odd
metastable levels	13 even	1 odd

[The odd metastable level is (^{3}F)4sp(^{3}P) $^5G_6$ at 27260.894 cm^{-1}.]

Hamiltonian parameters	2446 even	2996 odd
free LS parameters	33 even	33 odd
standard deviation	60 cm^{-1} even	88 cm^{-1} odd
total E1 lines saved	529632	old K88 149926
between known levels	9637	
total M1 lines saved	67880 even	159049 odd
between known levels	2227 even	5272 odd
betweem metastable	41 even	0 odd
total E2 lines saved	453222 even	929692 odd
between known levels	3776 even	7539 odd
between metastable	24 even	0 odd

isotope	^{56}Ni	^{57}Ni	^{58}Ni	^{59}Ni	^{60}Ni	^{61}Ni	^{62}Ni	^{63}Ni	^{64}Ni
fraction	.0	.0	.6827	.0	.2790	.0113	.0359	.0	.0091

There are 5 stable isotopes. There are measured splittings for 326 lines from which I determined 131 energy levels relative to the ground. These levels are connected by **11670 isotopic lines**. Hyperfine splitting was included for 61Ni but only 6 levels have been measured which produce 4 lines with 38 components. A pure isotope laboratory analysis is needed.

Ni I lines are asymmetric from the splitting. When the isotopic calculation was first checked against the solar spectrum it did not look right. Subsequently, I found a program error and recomputed the splittings. Now the profiles match the observed. Observed stellar spectra are generally not high enough quality to show that there are such errors.

Co I

Co I based on Pickering and Thorne (1996) [9] and on Pickering (1996) with **hyperfine splitting** [10]. This calculation was made before my programs were expanded. I will rerun this with twice as many configurations.

configurations	32 even	32 odd
levels	3546 even	5870 odd
largest J matrix	748 even	1130 odd
known levels	139 even	223 odd
metastable levels	31 even	1 odd

[The odd metastable level is (^{4}F)4sp(^{3}P) z^{6}G$_{6.5}$ at 25138.806 cm^{-1}.]

Hamiltonian parameters	1446 even	1762 odd
free LS parameters	27 even	26 odd
standard deviation	129 cm^{-1} even	126 cm^{-1} odd
total E1 lines saved	1729299	old K88 546130
between known levels	15481	
total M1 lines saved	396174 even	602458 odd
between known levels	3497 even	11993 odd
betweem metastable	286 even	0 odd
total E2 lines saved	1218019 even	2468646 odd
between known levels	5094 even	15943 odd
between metastable	410 even	0 odd

isotopic components	^{56}Co	^{57}Co	^{58}Co	^{59}Co
fractional abundances	.0	.0	.0	1.00

^{59}Co is the only stable isotope. Hyperfine constants have been measured in 297 levels which produce **244264 component E1 lines**. I have not yet computed the M1 or E2 components. The new calculation greatly improves the appearance of the Co I lines in the solar spectrum.

U I

In this volume, Wyart and Hubbard describe their web site for actinides. The U I directory is a good example of what can be accomplished with hard work. There are 1426 even levels and 536 odd levels, many with Landé g and isotopic splitting U^{238}-U^{235}.

Cr IV, Mn IV-V, Fe IV-VI, Co IV-VII, Ni IV-VIII

Sugar and Corliss (1985) [11] found no laboratory energy levels for n = 5, 6, 7, 8, 9 for these ions. The laboratory sources used were not able to populate the high upper levels to produce emission lines. However in hot stars lines to the excited levels appear in absorption shortward of Lyman α and through the Lyman continuum. For absorption it is necessary to populate only the lower level of a transition. The observed lines cannot be identified or analyzed. When I compute all these excited levels the uncertainty in the energies is too great. This is a problem that has to be solved by building new laboratory sources and by measuring the spectrum from the infrared to the extreme ultraviolet.

TiO

Schwenke calculated energy levels for TiO including in the Hamiltonian the 20 lowest vibration states of the 13 lowest electronic states of TiO (singlets a, b, c, d, f, g, h and triplets X, A, B, C, D, E) and their interactions. He determined parameters by fitting the observed energies or by computing theoretical values. Using Langhoff's transition moments [12] Schwenke generated a linelist for J = 0 to 300 for the

isotopomers	$^{46}Ti^{16}O$	$^{47}Ti^{16}O$	$^{48}Ti^{16}O$	$^{49}Ti^{16}O$	$^{50}Ti^{16}$
fractional abundances	.080	.073	.738	.055	.054 .

My version has 37744499 lines.

Good laboratory analyses and a similar semiempirical treatment are needed for CaOH, ScO, VO, YO, ZrO, LaO, etc. Better laboratory data could be used to further improve TiO.

I_2

I_2 is not an astronomical molecule but it is dear to the hearts of people who search for planets [13]. I_2 absorption cells are the standard against which radial velocities are measured. The I_2 transmission spectrum [14] is imposed on the stellar spectrum by passing the light from the star through an absorption cell maintained at a constant temperatue above 300K. By various reduction techniques the motion of the stellar spectrum relative to the I_2 spectrum is determined as a function of time. Since thousands of lines are compared, weak signals can be found. However a problem that people ignore is that the resolved spectrum of I_2 has never been observed. $^{127}I_2$ has 1/3 the doppler width of $^{16}O_2$. The resolving power required is in the millions but FTS spectra are in the range 300000 to 500000. Observers have been using FTS I_2 templates to reduce their data but the templates are so underresolved that an FTS line that has a depth of 1/3 is black in reality. A number of techniques have produced high resolution spectra of I_2 [15] that show the hyperfine structure in small wavelength intervals. We need a list of all the hyperfine energy levels. It would be absolutely fabulous if someone then would write a computer program that can generate the resolved transmission spectrum of an I_2 absorption cell for any temperature.

REFERENCES

1. Schwenke, D.W., *Faraday Discussions* **109**, 321-334 (1998)
2. Partridge, H. and Schwenke, D.W. 1997. *J. Chem. Phys.* **106**, 4618-4639 (1997)
3. Kurucz, R.L., in *Trans. Internat. Astronomical Union* **XXB**, edited by M.McNally, Kluwer, Dordrecht, 1988, pp. 168-172. = K88
4. Cowan, R.D., *J. Opt. Soc. Am* **58**, 808-818 (1968)
5. Garstang, R.H., *Monthly Notices Royal Astron. Soc.* **124**, 321-341, (1962); *Comm. Univ. of London Obs.***57** (1962)
6. Johansson, S., *Physica Scripta* **18**, 217-265 (1978)
7. Rosberg, M., Litzén, U., and Johansson, S., *Monthly Notices Royal Astron. Soc.* **262**, L1-L5 (1993)
8. Litzén, U., Brault, J.W., and Thorne, A.P., *Physica Scripta* **47**, 628-673 (1993)
9. Pickering, J.C., *Astrophys. J. Supp.* **107**, 811-822 (1996)
10. Pickering, J.C. and Thorne, A.P., *Astrophys. J. Supp.* **107**, 761-809 (1996)
11. Sugar, J. and Corliss, C., *J. Phys. Chem. Ref. Data* **14, Supp. 2**(1985)
12. Langhoff, S.R., *Astrophys. J.* **481**, 1007-1015 (1997)
13. Marcy, G.W. and Butler, R.P., *Pub. Astron. Soc. Pacific* **104**, 270-277 (1992)
14. Gerstenkorn, S. and Luc, P. *Atlas du Spectre d'Absorption de la Molecule de l'Iode (14800-20000 cm^{-1})*, C.N.R.S., Paris, 1978.
15. Sansonetti, C.J., *J. Opt. Soc. Am. B* **14**, 1913-1920 (1997)