

Using an Advanced Computational Laboratory Experiment To Extend and Deepen Physical Chemistry Students' Understanding of Atomic Structure

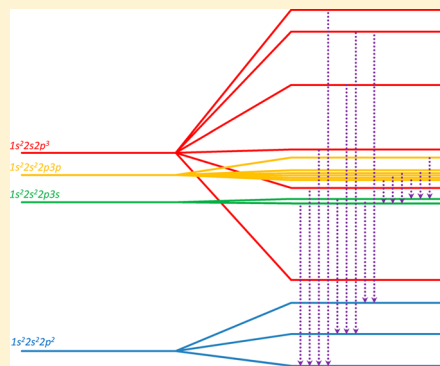
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S Supporting Information

ABSTRACT: A computational laboratory experiment is described, which involves the advanced study of an atomic system. The students use concepts and techniques typically covered in a physical chemistry course but extend those concepts and techniques to more complex situations. The students get a chance to explore the study of atomic states and perform calculations at a high enough level to provide predicted emission lines in good agreement with literature results. The specific exercise described applies these methods to fifth period transition metals (ground-state systems) and to various configurations of several period two representative elements (both ground and excited states). The computations are performed with programs written by Froese Fisher and co-workers, which perform Hartree–Fock (HF), multiconfiguration HF, and configuration interaction calculations. Since these are atomic systems, the angular dependence of the orbital functions can be described by spherical harmonics (or combinations thereof), which leaves a differential equation in the radial coordinate that can be solved by numerical methods. The details involved in this exercise are presented along with some typical results.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Laboratory Instruction, Computer-Based Learning, Hands-On Learning/Manipulatives, Atomic Properties/Structure, Computational Chemistry, Quantum Chemistry



INTRODUCTION

Electronic structure calculations are performed in all areas of chemistry research, and for this reason, it is important that undergraduate students gain some experience in this area. The formalism is taught in the traditional physical chemistry course where simple exercises are provided to illustrate some of the important concepts. However, a true appreciation of the field comes from laboratory work where the student can experiment with the parameters and work toward obtaining reliable results for the problem at hand. It is not uncommon to incorporate electronic structure calculations into physical chemistry laboratory exercises. The results of such calculations may help to guide the experimental work, or they may be used to explain the results obtained in the lab. Alternatively, the experiment may focus directly on the computational procedure itself and the value of the results gauged by comparison with experimental data.

Atomic systems are an attractive target for computational work because they allow some considerable simplifications in the equations of motion. The orbital functions are all centered on the single nucleus, and the angular portions of these functions can be modeled well with spherical harmonics. The solution of the Hartree–Fock (HF) equations for the helium atom ground state is particularly simple in that both electrons are described by the same orbital function, and these functions are spherically symmetric. There results a single differential

equation in a single variable. Exercises can be found in the chemical education literature that guide students through the solution of this equation using basis sets^{1,2} or numerical integration methods.³ A recent example⁴ investigates the solution of the analogous equation that arises with density functional calculations. Larger atoms are more complicated, but considerable simplifications are still possible. Spherical harmonics can still be introduced to describe the angular degrees of freedom, leaving differential equations in the remaining radial coordinate. Powerful numerical methods can be applied to solve these equations (with no need to introduce basis functions), and code to perform these calculations has been generated by Froese Fisher and co-workers.⁵

The exercise presented in this paper involves the investigation of an atomic system using accurate computational methods. To gauge the quality of the results, the students predict atomic emission spectrum lines and compare their predictions with literature values. Briefly, this experiment has students generate a set of acceptable electron configurations for a many-electron atom, generate the associated term symbols for those configurations, perform electronic structure calculations on the generated terms, use the computed energies to calculate wavelengths for the possible transitions, use the spectroscopic selection rules to predict the lines that should appear in an

atomic spectrum, and compare those predictions with experimental data.

The exercise builds on concepts and techniques already covered in a traditional physical chemistry course but goes well beyond the simple cases typically presented in the lecture course. For example, the student should be familiar with the idea of electron configurations. The focus in the classroom, however, is with ground-state configurations, and the student may not fully appreciate the construction of electron configurations for excited states as well. Further, the student should be familiar with generating the term symbols associated with an electron configuration,^{6–9} but the lecture course again focuses on the ground-state configuration. Situations where there is more than one open shell typically do not arise in the lecture course, and this exercise provides a learning experience in this respect. It is also common in the undergraduate physical chemistry course to present atomic spectroscopy and the associated selection rules.^{6,8,10,11} Some simple cases may be posed as problems, and the student can predict which transitions may or may not occur. This exercise goes well beyond these simple cases and illustrates several complicating factors; another learning experience is gained. Finally, the student is most likely exposed to the HF approximation and the notion that corrections are necessary for accurate work. The specifics associated with multiconfigurational HF (MCHF) and configuration interaction (CI) may not be as familiar, and the student will learn about these techniques first-hand. Even though the concepts used in this exercise may be already familiar to the student, the situations encountered will be considerably more in-depth. The student will have to wrestle with the concepts and, it is hoped, gain a deeper understanding and appreciation of them. There is also the chance of experimenting with the input parameters to see how they affect the results obtained.

This paper will present a particular way in which the exercise may be performed. There are many possible variations, though. Such variations will be discussed later.

■ THE EXERCISE

Overview

This exercise was originally designed to be covered in four classes. One may note, though, that this may be modified. For instance, part (or all) of the lecture portion of this exercise may be transferred to the lecture portion of the course, which would allow the laboratory portion to be covered in fewer class meetings, if desired. Further, some material may be left out or streamlined, which would also lead to fewer classes. Before getting to the specifics of the assignment, an overview of the original exercise will be presented. The exercise can be broken up into two main tasks, and it is useful to first present a general description of these tasks. This overview will be followed up with the technical details that are associated with each of those tasks.

The first task is the study of a transition metal element, the objective being to predict the appropriate ground state electron configuration. This task gives the student a chance to learn how to use the electronic structure programs on a relatively simple system. To make it interesting, there is a specific question to answer. Electronic structure calculations are performed for the configurations in which two, one, or zero electrons are in the valence *s* orbitals of the transition metal element, and the job is to determine which configuration yields the lowest energy. At

the start, the student will need to identify the lowest energy term symbol for each configuration and then perform the associated electronic structure calculations. Each student is assigned a different element. The fifth period has a number of anomalous configurations, and elements in this row have typically been assigned for study. Elements in other rows, of course, are equally appropriate. This is a straightforward and quickly achieved task and serves as a vehicle to get the students exposed to the necessary tools for studying atomic systems. They will encounter some difficulties but should be able to overcome them with minimal effort and achieve some positive results before they move on to the more challenging second task.

The second task is the study of a set of states for a representative element and the possible emission transitions among those states. In addition to the ground-state configuration, several low-lying excited-state configurations are assigned for which the student must generate all of the associated term symbols. There is little exposure to excited states for many-electron atoms in the typical physical chemistry course, and this exercise is a good remedy for this. For all of the terms, electronic structure calculations (to be described below) are performed to obtain the associated energies. By applying the selection rules, the allowed spectral transitions among the assigned configurations are predicted and compared with data from the literature. Each student is assigned a different atom for study. Because of the large number of experimental spectroscopic lines available and the relative simplicity of the associated calculations, representative elements in the second period have typically been assigned. The neutral atoms of the elements carbon, nitrogen, oxygen, and fluorine are sufficiently challenging. In addition, numerous cations with the same electronic configurations as these four are appropriate targets for study. The other elements, of course, and many other electron configurations may be chosen as well.

The exercise is carried out in stages, the necessary tools are presented one at a time, and the students generate their data as they go. Difficulties arise at various points, and the students learn how to deal with them as they move on. At the end, they write up a formal report on the results of their calculations.

Technical Details

The generation of the configurations and term symbols requires just pencil and paper (and patience). An industrious student may be able to write a program to generate the appropriate term symbols, and such a solution is encouraged. For the atomic structure calculations, the numerical programs developed by Froese Fisher and co-workers have been used. These programs are described in a book⁵ and may be downloaded from the NIST Web site.¹² These programs are written in Fortran 77 and must be compiled before use. These programs were installed on an Alpha workstation running Tru64 UNIX to which the students connect over the Web. They must learn some basic UNIX commands and some detailed instructions for running the programs and reading the output. This has not been a hindrance, however. Some students are actually enthusiastic about learning these things.

Specific details associated with the tasks are contained in two handouts, which are contained in the Supporting Information for this paper. The following sections present a detailed structure for a four-class sequence of lectures and tasks. As mentioned previously, this can be revised by presenting lectures in another class or by streamlining (or augmenting) the tasks.

First Class

A handout (Atomic states and spectroscopic transitions between them, see the Supporting Information) is provided to the students at or before the first class. This handout contains much of the detail covered in the lecture for the first class and is provided to make sure the students have the details right when they try to apply the associated material to their atoms. The lecture component is a prominent part of this class. The particular material covered is spectroscopy in general, atomic structure, electron configurations for many-electron atoms, and the determination of term symbols. The students are assigned their transition metal element and their representative element atom or ion. The tasks to be completed for the next class are as follows.

- (1) The generation of the lowest energy term symbols for the transition metal element in the $5s^24d^n$, $5s4d^{n+1}$, and $4d^{n+2}$ configurations (assuming a fifth period element is chosen). It is important to stress that only the lowest energy term symbol is needed for this task. Generation of all the term symbols for a transition metal is rather forbidding, and there are shortcuts when only the lowest energy term is needed.
- (2) The generation of all possible term symbols for the representative element atom or ion (assuming a second row element) in
 - (2a) the ground-state configuration,
 - (2b) the excited-state configuration obtained by promoting a $2s$ electron in the ground state to a $2p$ orbital,
 - (2c) the excited-state configuration obtained by promoting a $2p$ electron in the ground state to a $3s$ orbital, and
 - (2d) the excited-state configuration obtained by promoting a $2p$ electron in the ground state to a $3p$ orbital.

Second Class

The second class begins with the students presenting the results of the assignment. After clearing up any confusion that might have arisen, there is a lecture on atomic spectroscopy and the associated selection rules. The students are given the task of identifying all of the allowed transitions among the configurations generated for their representative element. They are also asked to look up all the experimental lines associated with these configurations. The NIST Web site is recommended for finding these data.¹³ It is pointed out that some of the allowed transitions may be missing from the experimental data and that some forbidden transitions may be present.

In carrying out this part of the assignment, many students will try a brute force approach, which works but can be rather time-consuming. It is possible to organize the task to eliminate large sets of transitions at a time. For instance, all transitions between cases 2b and 2c above can be eliminated with the appropriate selection rule. The students also may need some help downloading the data efficiently from the NIST Web site. The instructor provides guidance, as needed, for transferring the data and organizing it in an Excel spreadsheet.

At this class, a second handout is distributed (Electronic structure calculations on atoms, see the Supporting Information). This handout covers much of the material to be presented at the next class. It also describes, in full detail, how to run the programs for performing the atomic electronic structure calculations.

Third Class

The third class starts with a discussion of the results obtained from the last assignment, and a lecture on electronic structure theory is now given. This topic is covered briefly in physical chemistry lecture but will most likely need to be augmented for the task at hand. Relativistic contributions are presented (very briefly) as well as spin-orbit coupling. The HF approximation is presented (which should be review of material presented in the physical chemistry lecture course) and the concept of dynamical correlation introduced (which may or may not be a review). The construction of Slater determinant configurations and the expansion of the wave function in terms of these quantities is presented. The application of the variational principle leading to the (a) MCHF and (b) CI methods is then described. The concept of an *active space* and its choice is also discussed. In the end, the students should understand that they will be performing HF, MCHF, and CI calculations on their systems. The role of the quantum numbers L , S , and J in the calculations is discussed and where they need to be specified in the electronic structure calculations. The programs used perform the calculations by numerical quadrature, so there is no need to introduce basis sets.

The students are given a walkthrough of the computational procedure (it is fully presented in the handout). HF calculations are performed in a straightforward way with a program called *HF*. These calculations require specification of only the electron configuration and the L and S quantum numbers. The program presents both nonrelativistic and relativistic results (including corrections up to order $1/c^2$). The students are asked to record both values. After this, the higher-order calculations are set up. The first step is to generate the set of configurations needed for the remaining calculations. A program called *Gencl* is run that takes as input the reference configuration, the values of L and S , and the active space. The choice of active space is discussed to some extent, and the message is given that a good choice for the representative elements is the $n = 2$ and $n = 3$ orbitals (corresponding to $2s$, $2p$, $3s$, $3p$, and $3d$). It is also noted that they may have to experiment with this for some cases. The next program, *Breit*, computes a set of integrals associated with the configurations and writes them to a file. By using the orbitals generated by the HF calculation, then, an MCHF calculation is performed with a program called *MCHF*. The input for this is pretty much the same as for the HF calculation. The configuration list and integral values are read in by the program for this calculation. The main purpose of this computation is to generate a set of orbital functions to be used in the subsequent CI calculations. Even so, the students are asked to record the MCHF energy for each of the states. Finally, a CI calculation is performed with the program *CI*, which generates the states and energies for the different J values associated with the L and S values of interest.

After the walkthrough, the students are directed to perform calculations on the terms they generated for both the transition metal and the representative element. The transition metal calculations are to be presented at the next class.

Fourth Class

At the start of the fourth class, the students write their results for the transition metal on the board. The students are asked to predict the ground-state configuration and term symbol for their element at the (1) HF nonrelativistic level, (2) HF relativistic level, (3) MCHF level, and (4) CI level. With this activity, it is possible to identify problems that students are

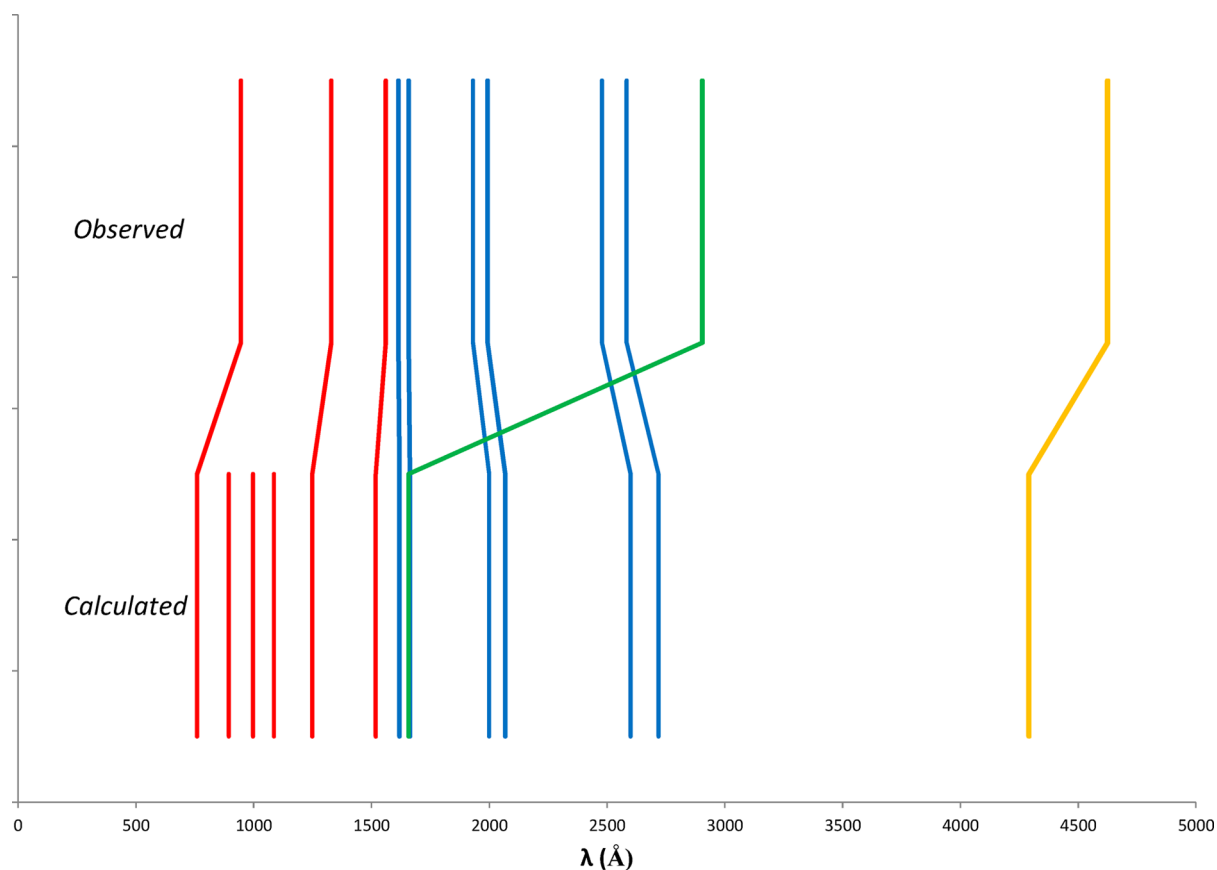


Figure 1. Comparison of experimental (top) and calculated (bottom) spectral lines at wavelengths below 5000 Å for carbon. The red lines correspond to transitions from the $1s^2 2s^2 2p^2$ states to the $1s^2 2s 2p^3$ states, the blue lines to transitions from the $1s^2 2s^2 2p^2$ states to the $1s^2 2s^2 2p^3$ states, the gold lines to the forbidden transitions from the $1s^2 2s^2 2p^2$ states to the $1s^2 2s^2 2p^2$ states, and the green lines to the forbidden transitions from the $1s^2 2s^2 2p^3$ states to the $1s^2 2s 2p^3$ states.

having before they get too far on the more involved project. The class is then turned over to a discussion of the computations performed so far. Students are asked about any specific difficulties they encountered. Some problem situations are typically mentioned. This provides the instructor a chance to discuss these situations and how they are to be dealt with. The problem cases and how to deal with them are actually described in the handout, and this is enough for the better students. However, it is worthwhile to explicitly mention those issues in class.

There are several specific difficulties that arise. First, nonconvergence is sometimes encountered in the HF and MCHF calculations. The procedure for continuing the calculation to achieve convergence is described. Second, configurations that have more than one of the same term designation (for instance, the $2s^2 2p^3 3p$ configuration of oxygen has three distinct sets of 3P terms) require a distinction of these terms. This is done by specifying the parent term, and a means of generating the possible parent terms is described. Third, the need is emphasized for checking the CI output to make sure the energy for the desired state is extracted. Finally, the possible requirement for modifying the active space for some cases is noted, and a procedure for this is described. The students are directed to finish the calculations, compare their results with experimental data, and discuss those results in a formal report.

TYPICAL RESULTS

Once the procedure for performing the atomic structure calculations has been mastered, the calculations go fairly quickly. Many students end up being able to perform a computation with a rapid series of memorized keystrokes. The transition metal calculations predict the accepted electron configuration at the CI level in all cases studied (the fifth period transition metals from Mo to Ag) except for Pd. The prediction based on HF (nonrelativistic), HF (relativistic), and MCHF calculations almost always agrees with the CI results. Curiously, for Pd, all the levels of calculations besides CI predict the accepted electron configuration.

The representative element calculations require more effort. Ignoring J values, there are 17 LS terms for carbon, 21 for nitrogen, 25 for oxygen, and 17 for fluorine. Each of these LS terms requires a separate set of calculations. Without any complications, these can all be performed in 2–3 h. Very often, however, problems arise, and the student will have to spend some extra time wrestling with finding solutions for these cases. The calculations will normally take more than one laboratory period but not more than two. A lot of this depends on the student. In the end, as long as a reasonable active space is chosen, the predicted spectral lines agree rather well with the literature data, differences in wavelengths mostly being less than 2%. Occasionally, there are some considerable differences, and these can usually be associated with one or maybe a few particular states. For instance, the transitions for the carbon atom having wavelengths less than 5000 Å are presented in

Figure 1. These calculations used an active space consisting of the $2s$, $2p$, $3s$, $3p$, and $3d$ orbitals. For the most part, the observed and predicted lines agree well. However, there is a set of three closely spaced lines that are considerably different. They are calculated to be at about $1657 \text{ \AA}$ but observed to be at about $2905 \text{ \AA}$. These three lines involve transitions between the 3P terms of the $1s^2 2s^2 2p^3$ configuration and the 3S_1 term of the $1s^2 2s 2p^3$ configuration for this atom. By probing a bit more deeply, it is noted that other transitions that involve the 3S_1 term are found to differ noticeably from the experimental data, while those of the 3P terms do not. The conclusion can be drawn that the calculation for the 3S_1 term of the $1s^2 2s 2p^3$ configuration for some reason falls short. This is the type of analysis expected of the students and the type of conclusion to be drawn. It would be unreasonable to expect anything deeper than this (such as the need for a second reference configuration) from an undergraduate, but some exceptional students may make the leap.

There is a lot of bookkeeping in this exercise. The energies for all of the states must be computed and used to compute the wavelengths for all the transitions. For the exercise outlined above, there are 44 allowed transitions and 60 forbidden transitions found for carbon on the NIST Web site. Similarly, there are 103 allowed transitions and 43 forbidden transitions for nitrogen, 120 allowed transitions and 27 forbidden transitions for oxygen, and 27 allowed transitions and 1 forbidden transition for fluorine. The use of a spreadsheet program is virtually required. While students may grumble about the tedium involved, they perform the tasks and some even exhibit a certain amount of pride in successfully tabulating the data and generating spectra that agree favorably with the experiment.

VARIATIONS AND EXTENSIONS

There are many variations that can be applied to this exercise. It may be applied to most of the elements. It may be applied to neutral or charged species. It may be applied to a large number of possible electron configurations. Each student may be assigned a different atom or ion, or a group of students may be assigned to the same element but different configurations. It is possible, with a large enough class, to try to predict a spectrum for a single element, boron for instance. One may assess the effect of modifying the active space on the calculations. How much of an effect does the addition of certain orbital subshells actually have? It may also be possible to generate an atomic spectrum in the laboratory and try to assign the lines observed.

CONCLUSIONS

A computational laboratory experiment has been described that allows students to apply techniques and concepts learned in the typical physical chemistry course to a system of considerable complexity. They perform electronic structure calculations of some sophistication and compare their results to literature data. For the most part, the comparison with the literature is rather good and leads to a feeling of confidence in performing electronic structure calculations and their use in laboratory work. A number of possible extensions have also been suggested.

ASSOCIATED CONTENT

Supporting Information

Two laboratory handouts: atomic states and spectroscopic transitions between them, and electronic structure calculations on atoms. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Snow, R. L.; Bills, J. L. A Simple Illustration of the SCF-LCAO-MO Method. *J. Chem. Educ.* **1975**, *52*, 506–509.
- (2) Rioux, F. An Interactive SCF Calculation. *J. Chem. Educ.* **1994**, *71*, 781–782.
- (3) Hoffman, G. G. Self-Consistent Field Calculations on Atoms Using Excel. *J. Chem. Educ.* **2005**, *82*, 1418–1422.
- (4) Baseden, K. A.; Tye, J. W. Introduction to Density Functional Theory: Calculations by Hand on the Helium Atom. *J. Chem. Educ.* **2014**, *91*, 2116–2123.
- (5) Froese Fischer, C.; Brage, T.; Jönsson, P. *Computational Atomic Structure: An MCHF Approach*; Institute of Physics Publishing: Bristol, UK, 1997.
- (6) Dykstra, C. E. *Physical Chemistry: A Modern Introduction*; Prentice Hall: Upper Saddle River, NJ, 1997.
- (7) Engel, T. *Quantum Chemistry and Spectroscopy*; Pearson, Benjamin Cummings: San Francisco, CA, 2006.
- (8) McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, 1997.
- (9) Raff, L. M. *Principles of Physical Chemistry*; Prentice Hall: Upper Saddle River, NJ, 2001.
- (10) Mortimer, R. G. *Physical Chemistry*, 2nd ed.; Harcourt, Academic Press: San Diego, CA, 2000.
- (11) Silbey, R. J.; Alberty, R. A. *Physical Chemistry*, 3rd ed.; John Wiley & Sons, Inc.: New York, 2001.
- (12) See, in particular, the following URL. It is necessary to accept a license agreement before proceeding to the page for downloads. After proceeding to the new page, go to the bottom and press the link labeled “Download ATSP”. This will download a gzipped tar-file that contains all the necessary programs. <http://nlte.nist.gov/cgi-bin/MCHF/download.pl?d=ATSP>, accessed Feb. 25, 2015.
- (13) *NIST Atomic Spectra Database*; The National Institute of Standards and Technology: Gaithersburg, MD, 2014. <http://nist.gov/pml/data/asd.cfm> (accessed January 2015).