

CRITICAL EVALUATION OF DATA ON ATOMIC ENERGY LEVELS, WAVELENGTHS, AND TRANSITION PROBABILITIES

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Current methods of critical evaluation of wavelengths, energy levels, and transition probabilities for atoms and atomic ions at the National Institute of Standards and Technology are summarized.

KEYWORDS: *atomic data evaluation, energy levels, transition probabilities*

Note: Some figures in this paper are in color only in the electronic version.

I. INTRODUCTION

At the National Institute of Standards and Technology (NIST), we are carrying out a systematic program of critical compilation of wavelengths, energy levels, and transition probabilities of atoms and atomic ions.

For the most part, the evaluated data on wavelengths and energy levels are experimental values based on laboratory observations. In some cases, such as for H-like and He-like ions, the data are derived from calculations with sophisticated atomic structure codes that include relativistic and quantum electrodynamic effects. For transition probabilities, the situation is reversed. Most of the data come from theoretical calculations, but some are experimentally measured in laboratory or astrophysical spectra.

The process of producing a critical compilation requires retrieval of all data from the literature for a particular ion. It is important to have a complete bibliography for the considered spectrum. For this purpose, we use the NIST Atomic Energy Levels and Spectra Bibliographic Database¹ and the NIST Atomic Transition Probabilities Bibliographic Database.² Both of these databases are maintained up-to-date. In addition to these databases, it is worthwhile to query the BIBL database³ of the Institute of Spectroscopy, Troitsk, Russia. This database is updated twice a year and is independent of the NIST databases. Quite often, some papers missed in the NIST

database may be present in the BIBL database. For completeness, these bibliographic searches should be complemented by examining the references in the papers found and by searching in other available Internet resources.

In many cases the data must be extracted from more than one paper. For neutral and moderately ionized atoms, it is not uncommon for 10 or more papers to be used. Often the data from different papers are inconsistent, and possibly contradictory. Where possible, we attempt to resolve these conflicts by use of isoelectronic comparisons, analysis of Rydberg series, and *ab initio* or semi-empirical calculations. In some cases level identifications given in the literature are incomplete in their specifications, and new calculations are needed to obtain appropriate names. If available, we tabulate the percentage compositions for the observed levels. In many cases these compositions are taken from our own calculations.

When data from two or more papers are blended together to form a single list of lines and levels, it is usually necessary to derive a new set of levels and to optimize their values so that the Ritz wave numbers (differences of the level values) best reproduce the observed spectrum. This is usually done with a computer code that weights the wave numbers according to their uncertainties and minimizes the differences between the observed wave numbers and those derived from the levels in an iterative procedure. The final Ritz wavelengths are usually more accurate than those that were observed.

To provide a complete description of the energy structure of an atomic spectrum, it is often necessary for us to

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determine an ionization energy (IE) from the observed data. Several methods have been developed for this purpose as well as for other aspects of the compilation process.

Since experimental data on wavelengths and energy levels are usually of high precision, several strict numerical procedures exist that allow us to detect inconsistencies in the data and select the best available data that fit together in a coherent picture. The process of critical evaluation of such data is well structured and developed.

On the other hand, the data on transition probabilities are usually much less accurate and more difficult to analyze. The process of critical evaluation of these data strongly depends on the methods used to produce them and on availability of other independently obtained data for comparison. At NIST, we have developed several methods that can be used for evaluation of transition probability data.

The methods we use are briefly reviewed in the following sections.

II. CRITICAL EVALUATION OF WAVELENGTHS AND ENERGY LEVELS

Figure 1 schematically illustrates the process of critically compiling wavelength and energy level data. This is a somewhat updated version of the procedure previously described by Reader.⁴ As can be seen, our independent calculations play an important role in nearly all aspects of the process. The example shown in Fig. 1 is for a case where two literature sources are being consulted. Although in practice there may be only a single source that is needed, more often there are many more that have to be blended together to form the final compilation.

II.A. Evaluation of Wavelengths

For each data source, the measured wavelengths have to be examined and, if necessary, corrected. The first thing to consider is the wavelength standards used. For old publications, the standard wavelengths may have been revised. If so, this revision has to be applied to the measured values. One of the many examples is the In II spectrum measured by Karlsson and Litzén⁵ using Fourier Transform spectroscopy (FTS). In this work, the wave number scale was calibrated by means of Ar II lines previously measured by Norlén.⁶ Nave and Sansonetti⁷ recently found that Norlén's wave number scale has a multiplicative calibration error. To correct for this error, all wave numbers from the Karlsson and Litzén⁵ paper have to be increased by 6.7 parts in 10^8 .

In many cases the number and quality of reference wavelengths is insufficient, and there remain some systematic shifts. They can often be eliminated by using, as internal standards, Ritz wavelengths based on independently derived accurate values of energy levels. As an example, Fig. 2 shows relative deviations of the original

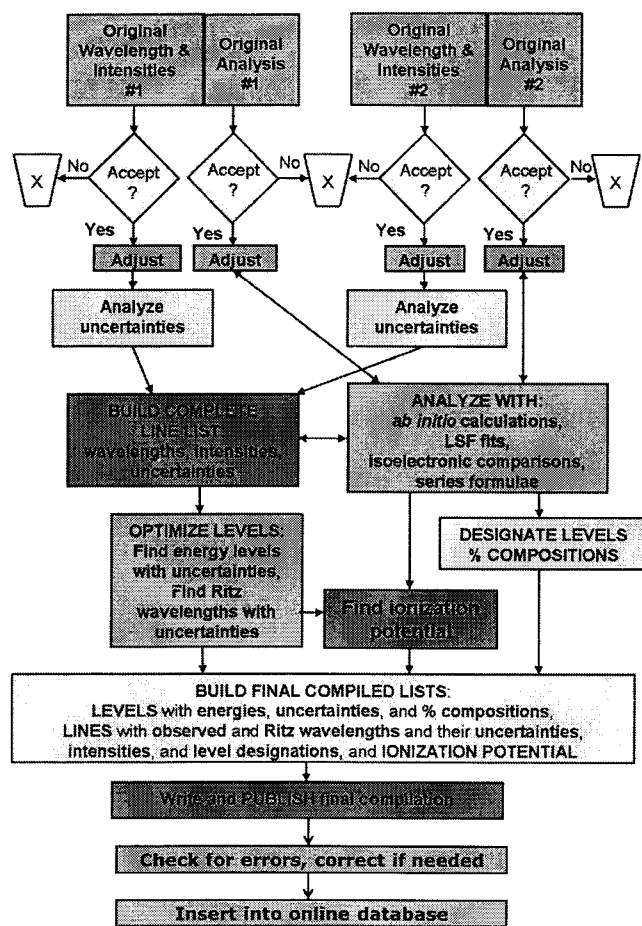


Fig. 1. Process of critical evaluation of data on wavelengths and energy levels.

Ag II wave numbers measured by Rasmussen⁸ from Ritz wave numbers based on FTS measurements of Kalus et al.⁹ plotted against the wave number.

As seen from Fig. 2, systematic shifts in Rasmussen's measurements are comparable to or exceed statistical uncertainties estimated from the scatter of data points around the smooth fitted curve. Removal of these systematic shifts leads to a more accurate determination of wavelengths corresponding to highly excited energy levels that were observed in the work of Rasmussen⁸ but were not observed by Kalus et al.⁹

Other systematic effects, such as pressure shifts and Stark shifts caused by external electric fields, have to be carefully considered, as was done, for example, in the recent work¹⁰ on $^{198}\text{Hg I}$.

II.B. Evaluation of Intensities of Spectral Lines

Observed relative intensities of spectral lines are usually only qualitative. They depend on the registration setup and on the light sources used. Nevertheless, they

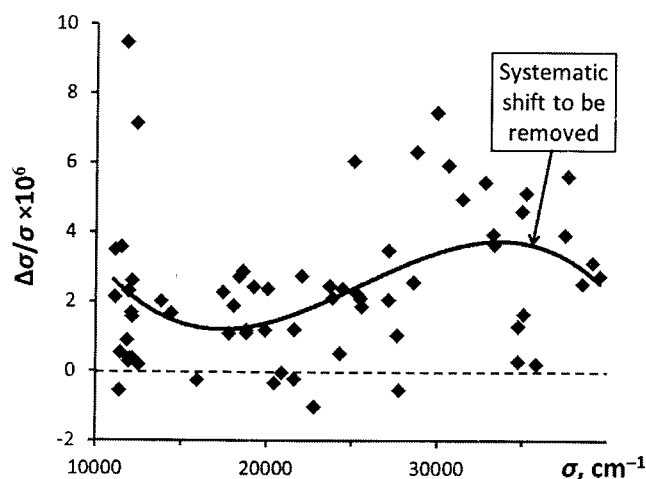


Fig. 2. Relative deviations of wave numbers measured by Rasmussen⁸ from Ritz wave numbers based on measurements of Kalus et al.⁹ The smooth curve is a cubic polynomial fit to the data points.

are important, because they provide a widely used qualitative criterion for line identification: Lines theoretically predicted to be strong should be strong in the observed spectrum. In many cases the wavelength measurement accuracy is insufficient to uniquely identify an observed line with a transition between a certain two energy levels, since there may be many possible transitions close to the observed wavelength. Comparison of observed relative intensities with theoretically modeled ones helps make a definite identification.

To facilitate comparisons of relative intensities observed with different registration equipment and different light sources, these intensities have to be reduced to a uniform scale. Such reduction is not always possible, but often it is. Effective excitation temperatures of the light sources can be derived from Boltzmann plots built using theoretical values of radiative rates. Approximate spectral response curves of the registration equipment can be derived by plotting the ratios of observed intensities and those calculated assuming the local thermodynamic equilibrium (LTE) in the light source. Then all observed intensities, corrected for the variation of sensitivity with wavelength, can be reduced to a common effective excitation temperature. These procedures were successfully applied to line intensities in the Ne II–IV (Ref. 11), In II (Ref. 12), and Ag II (Ref. 13) spectra. They are explained in detail in Ref. 12.

Of course, there exist more accurate methods of theoretical modeling of line intensities for non-LTE plasmas that take into account such aspects as level population kinetics including excitation/de-excitation, detailed ionization balance, self-absorption of radiation, etc. However, experimental details such as the intensity response calibration of the registration equipment and the precise geometry and excitation conditions of the light sources

are most often unavailable, making the application of such methods impossible. In addition, theoretical parameters required for such modeling (radiative rates and collisional cross sections) in most cases are not accurate enough to justify the effort. The approximate method outlined above usually gives relative intensities consistent with the assumption of LTE to within a factor of 3 on average.

II.C. Evaluation of Consistency of Analysis

The most important and easily implemented criterion of consistency of analysis is provided by the Ritz combination principle. It simply means that for each observed spectral line classified as a transition between two energy levels, the observed wave number must be equal to the Ritz value, which is the difference between the two energy levels within the stated measurement uncertainty. Some observed wave numbers may deviate from the Ritz values by more than one uncertainty, but the number of such outliers should not exceed $\sim 30\%$ of the total number of observed lines (assuming the uncertainties are given in terms of 1σ). Special considerations should be given to blended lines, including multiply classified lines. For such lines, deviations of observed wave numbers from Ritz values may be significantly greater.

One example of an inconsistent analysis recently has been found¹³ in the Ag II vacuum ultraviolet (VUV) spectrum reported by Benschop et al.¹⁴ These authors reported 64 newly identified spectral lines of Ag II between 1027 and 2034 Å. Half of these lines were associated with the previously unknown $4d^9 9s$ configuration and $4d^8 5s^2 \ ^1S_0$ level. Although only the newly identified lines were listed, the authors claimed that they confirmed and refined all levels previously reported by other authors, and they gave a complete revised level list. Since two coauthors of that paper, Y. N. Joshi and Th. A. M. Van Kleef, are respected spectroscopists who published several hundred papers on analyses of various atomic spectra, the results of this work were widely accepted and used by many authors (see, for example, Campos et al.¹⁵ and Morton¹⁶).

The measurement uncertainty stated by Benschop et al.¹⁴ for strong unblended lines was 0.005 Å. However, when the measured wave numbers are compared with the Ritz values derived from their energy levels (see Fig. 3), a striking inconsistency is revealed.

Normally, one would expect most of the observed wave numbers to differ from the Ritz values by no more than two times the measurement uncertainty. However, Fig. 3 shows the opposite: Most of the measured lines are outside this range. If the level values derived by Benschop et al.¹⁴ are replaced with much more accurate ones reported later by Kalus et al.,⁹ inconsistencies become even more drastic (see Fig. 4).

From Figs. 3 and 4, it is seen that deviations of observed wave numbers from Ritz values cannot be reduced

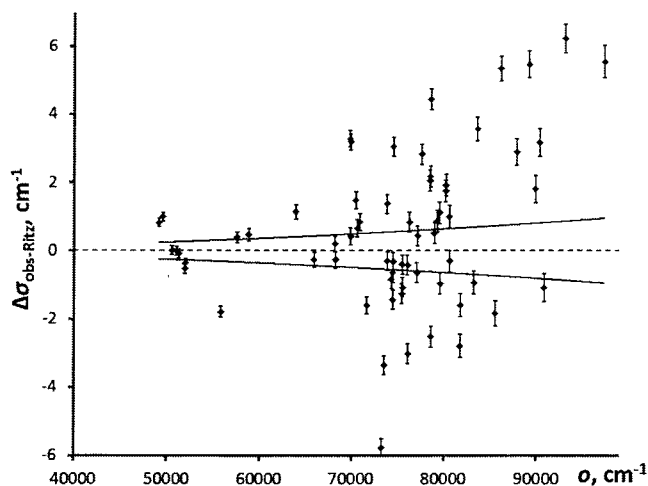


Fig. 3. Deviations of observed wave numbers from Ritz values for Ag II lines reported by Benschop et al.,¹⁴ with their energy levels. The horizontal axis is the wave number of the line. The error bars correspond to the measurement uncertainty of 0.005 Å. The smooth solid curves represent a difference from zero by two times the measurement uncertainty.

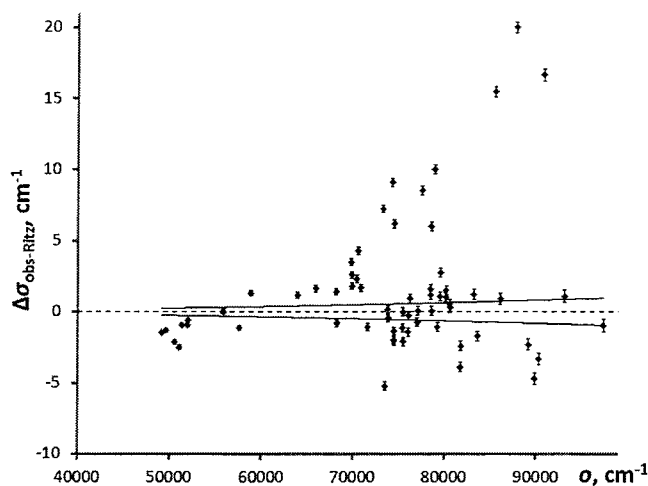


Fig. 4. Deviations of observed wave numbers from Ritz values for Ag II lines reported by Benschop et al.,¹⁴ with energy levels from Kalus et al.⁹ Uncertainty bars and solid curves are the same as in Fig. 3.

to the level of measurement uncertainties by applying any calibration correction function smoothly varying with wavelength.

In addition, the observed line intensities reported by Benschop et al.¹⁴ have no correlation with radiative rates, which I calculated¹³ using a parametric fitting with Cowan's codes.¹⁷ This can be seen in the Boltzmann plot shown in Fig. 5. No straight line with a negative slope can be fitted to data points on this plot, which means that

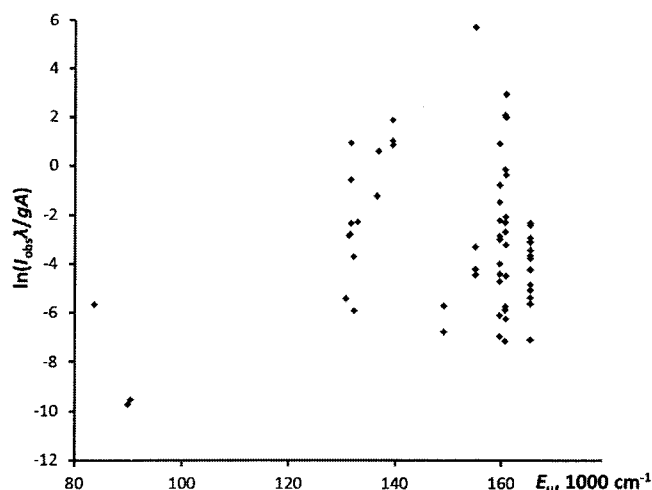


Fig. 5. Boltzmann plot of Ag II line intensities observed by Benschop et al.¹⁴

if the identifications are correct, the level populations cannot be approximated by LTE with any reasonable effective excitation temperature. This contradicts observations made with similar light sources in other spectra. (A sliding spark, triggered vacuum spark, and helium-filled hollow cathode discharge were used by Benschop et al.) No reasonable assumption about a smooth variation of the registration sensitivity with wavelength can rectify this Boltzmann plot.

Because of the above considerations, I concluded that the entire analysis of Benschop et al.¹⁴ is incorrect, and all their results must be discarded. This shows that even an established good reputation of the authors is insufficient for accepting their results.

Another important part of the evaluation of the consistency of analysis is comparison with independent theoretical calculations of reasonably high quality. Such calculations can be used not only in the analysis of line intensities illustrated above, but also in a more general view. For example, the number of energy levels assigned to a certain configuration should not exceed the number of possible levels predicted by quantum mechanics. If the coupling conditions are sufficiently pure (e.g., close to pure *LS* or *JJ* coupling), the splittings of levels within terms should conform to well-known rules. Observation of transitions that are normally strongly forbidden or that involve a simultaneous change of state of two or more electrons should be justified. For example, forbidden transitions can be observed in absorption or emission if their lower or upper levels, respectively, are metastable and accumulate a high population at the conditions of the experiment. Intercombination transitions and transitions involving two-electron jumps can be possible due to strong level mixing. This can be revealed by a theoretical calculation. If such calculations are unavailable in the literature, one should make them using available resources

and computer codes. In my practice, Cowan's codes¹⁷ were almost always sufficient for these purposes.

II.D. Level Optimization

Once a complete list of observed and identified spectral lines is built, it can be used to derive a set of energy levels that best fit the observed wave numbers. This is done in a procedure called least-squares level optimization. In this procedure, the observed wave numbers are weighted by squared reciprocal uncertainties. For this purpose, I recommend using my computer code LOPT.¹⁸ Although seemingly straightforward, level optimization has many subtleties and pitfalls. Some of them are explained in the paper cited above, along with recipes for avoiding them and practical examples.

The crucial factor in any level optimization is the validity of all line identifications. Incorrect identifications invalidate the entire procedure.

The most important subtlety is in the difference between the notions of transition and spectral line. The quantities that must be used in the input of the level optimization procedure are *transition* wavelengths or wave numbers along with their measurement uncertainties. However, the quantities actually measured are wavelengths or wave numbers of centers of *spectral lines*. A spectral line does not necessarily arise from a single transition but can be a blend of several transitions. Thus, for the purpose of level optimization, measurement uncertainties of blended lines must be greatly increased, because an individual transition assigned to such a line can be located anywhere within the profile of the line. Sometimes blended line profiles can be decomposed into individual components; this could possibly remove the requirement of increased uncertainties.

Another important point is that the least-squares level optimization procedure is statistically rigorous only in the absence of systematic effects such as calibration errors. Thus, all known systematic effects should be removed from the measured values prior to deriving the energy levels. In many spectra there are ladderlike systems of energy levels having multiple transitions in the visible or infrared regions of spectra where wavelengths can be measured with high precision. In such spectra, transitions from highly excited levels to the ground configuration usually lie in the VUV and rarely can be measured with accuracy comparable to that of the long-wavelength regions. It is common to use the Ritz wavelengths of such transitions as VUV wavelength standards. However, if there are any residual systematic shifts in the long-wavelength measurements used to determine the energy levels, these systematic shifts add up with each step of the ladder connecting highly excited upper levels to the ground configuration. The LOPT code has an effective way of estimating such systematic effects.

An important diagnostic parameter of the least-squares optimization is the residual sum of squares (RSS).

If the problem is posed statistically correctly (i.e., all input wavelengths are statistically independent, implying the absence of systematic effects), the ratio of RSS to the number of degrees of freedom of the problem (DF = number of measured transitions minus number of energy levels involved) must be close to unity. Another consistency test can be made by counting the number of outliers, i.e., the number of transitions for which the measured wavelength deviates from the Ritz value by a given multiple of the measurement uncertainty. For example, for a normal statistical distribution, the fraction of lines deviating from the Ritz values by more than one measurement uncertainty should be close to 32%; the fraction of lines deviating by two or more uncertainties should be about 5%, etc. If the number of outliers significantly exceeds these values, it is an indicator of some problems, either with identifications of transitions or with the measured wavelengths. In such cases the outliers should be carefully examined, and the problems resolved either by discarding the wrong identifications or by adjusting the wavelengths or their uncertainties. Such analysis should be made for each subset of data coming from separate experiments.

II.E. Deriving the Ionization Energy

Once the energy levels are firmly established and their uncertainties are assessed, they often can be used to derive spectroscopic values for the ionization limits. Such derivation can be made, for example, by using a series of levels converging to the same limit. For this purpose, I often use the nonlinear least-squares fitting computer code RITZPL developed by Sansonetti.¹⁹ This program fits a series of levels to the quantum-defect expansion formulas of the following types:

$$\delta_n = c_0 + c_1/(n - \delta_n)^2 + c_2/(n - \delta_n)^4 + c_3/(n - \delta_n)^6 + \dots \quad (1a)$$

or

$$\delta_n = c_0 + c_1/(n - c_0)^2 + c_2/(n - c_0)^4 + c_3/(n - c_0)^6 + \dots \quad (1b)$$

where c_i are the fitted constants and δ_n is the quantum defect describing an empirical correction to the principal quantum number n required for the excitation energy E_n to satisfy the hydrogenic formula:

$$E_I - E_n = RZ^2/(n - \delta_n)^2, \quad (2)$$

where

E_I = ionization energy

Z = charge of the ionic core

R = Rydberg constant.

The quantity $n^* = n - \delta_n$ is often referred to as the effective quantum number. Equation (1a) is called the extended Ritz formula, and Eq. (1b) is called the modified Ritz formula.

In highly ionized atoms, it is rare to have experimental values for many series members. In such situations, it is often possible to extrapolate some known values of the effective quantum number n^* from a similar well-known spectrum to the spectrum of interest and find a semiempirical value for the ionization limit from Eq. (2).

The quantum defect expansion Eqs. (1) and (2) are applicable only if the series is not perturbed by interactions with other series. Presence of such perturbations can be revealed by plotting the quantum defects along the series of n . If the dependence is not smooth, the series is perturbed. In such cases the limit can be found by using the multichannel quantum defect theory,²⁰ which is significantly more complex. Detecting perturbations and identifying their source is not always simple. Sometimes a deviation of a quantum defect from the smooth curve along the series indicates errors in line identifications or line blending. Theoretical ab initio or semiempirical calculations are essential in series analysis.

A good example of application of several different methods to derive an IE of a highly ionized atom was given by Reader et al.²¹ These authors derived the IE of Kr VIII from observed level series $[3d^{10}]ns, np, nd, nf, ng$, and ni . Quantum defect Eqs. (1) and (2) were used for series with low orbital quantum number (s, p, d). For the two observed members of the nf series ($n = 4, 5$), the IE was determined using a calculated value for the change in the effective quantum numbers of the two series members. This calculation was made ab initio with a multi-configuration Dirac-Fock (MCDF) method. For the high-orbital momentum series (ng and ni), a polarization formula discussed below was used.

If a series of levels with nonpenetrating external electron is known, then there is an alternative way of deriving the ionization limit, by using the polarization formula (see, for example, Sansonetti et al.²²):

$$E_n = E_I - T_H(n, l) - \Delta T_{pol}(n, l), \quad (3)$$

where $T_H(n, l)$ is the hydrogenic term value:

$$T_H(n, l) = \frac{Z^2 R}{n^2} \left[1 + \frac{\alpha^2 Z^2}{n^2} \left(\frac{n}{l + 1/2} - \frac{3}{4} \right) \right], \quad (4)$$

where α is the fine-structure constant.

The polarization contribution can be written as

$$\Delta T_{pol}(n, l) = R a_0 [\alpha'_d / \langle r^{-4}(n, l) \rangle + \alpha'_q / \langle r^{-6}(n, l) \rangle], \quad (5)$$

where

α'_d, α'_q = effective dipole and quadrupole polarizabilities of the core

a_0 = Bohr radius

$\langle r^{-4}(n, l) \rangle, \langle r^{-6}(n, l) \rangle$ = expectation values to be determined for the appropriate hydrogenic state using formulas given by Bockasten.²³

The polarization formula does not include fine-structure splitting but can be applied to the centers of gravity of terms.

Fitting of the polarization formula expressed by Eqs. (3), (4), and (5) was implemented in a computer code POLAR by Sansonetti.²⁴ It is as easy to use as the RITZPL code for the quantum defect formulas. All one has to do is specify the energies for the series levels, appropriate quantum numbers, and weights for each series member.

Another type of polarization formula was suggested by Schoenfeld et al.²⁵ It can be used for deriving ionization limits of complex spectra such as Fe II.²⁶

The series formulas can be used to interpolate and extrapolate energy levels along the series. In this way it is often possible to derive more accurate values than the experimental ones and to detect incorrect identifications. Of course, interpolations and extrapolations give correct results only in the absence of perturbations in the series.

Besides the series formulas, there are other semiempirical methods of deriving the IE. One example is the method of semiempirical adjustment of Cowan code calculations developed and applied to deriving IE for all stages of ionization of tungsten by Kramida and Reader.²⁷

II.F. Theoretical Interpretation of the Energy Levels

An important requirement for a critically evaluated set of energy levels is consistency of the level notation. In many cases various parts of the level system are analyzed by different authors using different naming conventions and different coupling schemes. In the final critically evaluated data set, a proper coupling scheme should be chosen that best describes the physical nature of the levels. Sometimes different subsets of electronic configurations are best described in different coupling schemes. For example, in Ne II the $2s^2 2p^4 nl$ configurations with $l = s, p, d$ are best described in the LS coupling, while for the $2s^2 2p^4 nl$ configurations with $l = f, g, h$, the JK coupling is the best.²⁸ However, giving one part of a configuration in one coupling scheme and another part in a different scheme is not physically meaningful. To find a proper notation, one has to perform atomic structure calculations.

For this purpose, I and other members of the NIST Atomic Data Center most often use Cowan's atomic structure code package.¹⁷ Although it is based on a nonrelativistic Hartree-Fock approximation with some relativistic corrections accounted for as perturbations, it has an important capability of semiempirical adjustment of effective Slater parameters by means of least-squares fitting (LSF) of known energy levels. It can account for the main configuration interactions, which are also introduced as perturbations. This approach has a proven record of success in atomic spectroscopy. *Ab initio* calculations with Cowan's codes are admittedly less accurate than some other existing approaches, such as the many-body perturbation theory (MBPT), relativistic configuration-interaction (RCI), and MCDF methods, to name a few. However, compared with these advanced methods, Cowan codes are much simpler and faster, and Cowan's LSF procedure¹⁷ in most cases yields an accuracy of energy levels with which no other presently available method can compete.

The LSF procedure is also effective in detecting spurious level identifications. Cowan's codes can calculate percentage compositions of eigenvectors in several coupling schemes, which is essential for choosing a correct notation for the energy levels.

II.G. Isoelectronic Comparisons

Isoelectronic interpolations or extrapolations are widely used to evaluate correctness of the analysis and sometimes can provide more accurate data than experimental measurements. The most accurate interpolations can be obtained by plotting the differences of experimental values from accurate theoretical calculations along an isoelectronic sequence. For example, in Ref. 29 I used the differences of observed energies of the $2s_{1/2}$ - $2p_{1/2}$ transition in Li-like ions from theoretical values calculated by Yerokhin et al.³⁰ to obtain an accurate wavelength for this transition in W^{71+} , 64.140(12) Å. Isoelectronic interpolations are safe only if the dependence of the interpolated quantity on the nuclear charge is known to be smooth. For example, level crossings, which often occur in isoelectronic sequences, destroy the smoothness of energy intervals and make interpolations unsafe. In such cases, it is often possible to interpolate other quantities that do behave smoothly along the sequence, for example, ratios of Slater parameters fitted by LSF to their Hartree-Fock values. This method was used, for example, in Ref. 31 to accurately predict energy levels of Be-like Si XI and to detect several errors in line identifications in Be-like ions.

III. CRITICAL EVALUATION OF TRANSITION PROBABILITIES

An excellent review of methods of critical assessment of transition probabilities (TP) was given earlier by

Wiese.³² He discussed in detail the following four main criteria used in this assessment:

1. consideration of the critical factors of a method by the authors
2. the authors' estimates of the uncertainty of their measured or calculated data
3. the degree of agreement with other reliable data, based on tabular or graphical comparisons
4. the fit of the data into systematic trends, or deviations from them.

I discuss below some additional aspects important for data assessment.

III.A. Matching Calculated TP with Experimental Energy Levels

As pointed out by Wiese,³² the majority of TP data come from theoretical calculations, while the majority of energy level data are experimental. The accuracy of the TP calculations greatly depends on the accuracy with which the model used approximates the experimental energy levels. In complex spectra, the density of levels is often so great that even the most elaborate theoretical calculation cannot reproduce the level separations or their ordering. Thus, it becomes nontrivial to establish a correspondence between the calculated and observed quantities. In this context, the crucial factor is the choice of characteristics defining the identity of a quantum state. As mentioned above, energy is not a good criterion of identity. For spectroscopists, an identity of a quantum state is defined by transitions in which it participates and by intensities of these transitions.

I recently discussed an example of this problem occurring in the Na II spectrum.³³ In this spectrum, some of the levels of the $2p^53d$ and $2p^54s$ configurations are very close to each other. They are highly mixed, and their ordering in theoretical calculations strongly depends on the approximation used. In this situation, comparison of relative intensities of lines originating from the same upper level with calculated transition probabilities provided a decisive criterion for identifying the experimental levels with theoretical ones. Such comparison is reliable in this case because it does not depend on modeling of the level populations and the relevant spectral lines are in a relatively narrow spectral range, where variation of the spectral response of the registration equipment is expected to be small.

Figure 6 illustrates this comparison for the case of the two levels with $J = 1$ at 333 107.74 and 333 162.94 cm^{-1} (see the recent NIST compilation³⁴). These levels were designated by Wu³⁵ as $2p^5(^2P^{\circ}_{1/2})3d\ ^2[3/2]_1$ and $2p^5(^2P^{\circ}_{1/2})4s\ ^2[1/2]_1$, respectively. In calculations of transition probabilities by Hibbert et al.,³⁶ these two levels are designated in *LS* coupling as $2p^53d\ ^3D^{\circ}_1$ and $2p^54s\ ^1P^{\circ}_1$, but the correspondence is uncertain

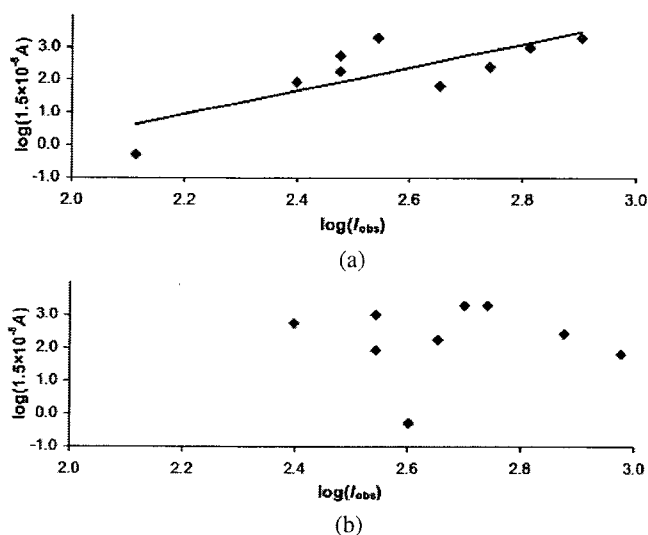


Fig. 6. Plots of $\log(A)$ versus $\log(I_{\text{obs}})$ for transitions from the two experimental Na II levels with $J = 1$ at 333 107.74 and 333 162.94 cm^{-1} . The A values were calculated by Hibbert et al.³⁶ for transitions from the $2p^53d^3D^{\circ}_1$ level to all $2p^53p$ levels. (a) Assumption that the $3d^3D^{\circ}_1$ level is the upper of the two experimental levels; (b) assumption that it is the lower level. Adapted from Ref. 33.

because of the closeness of the levels. The two panels of Fig. 6 test the two possible assumptions about the level ordering. In Fig. 6a, the theoretical $3d^3D^{\circ}_1$ level is assumed to correspond to the upper of the two experimental levels, while in Fig. 6b it is assumed to be the lower one. The correct identification should be the one for which the observed line intensities are proportional to the calculated A values.

Comparison of Fig. 6a and Fig. 6b leads to an unambiguous conclusion that the upper of the two experimental levels is the $3d$ one. This means that Wu's assignment of this level to the $2p^54s$ configuration³⁵ was incorrect.

An essential detail of Fig. 6 is the use of the logarithmic scales for both the calculated A values and the observed line intensities. This use of the logarithmic scale is a rule for such comparisons, as well as for comparisons of different calculations of transition probabilities with each other. It is dictated by statistical properties of both theoretical calculations and measurements of line strengths. Even in a very accurate calculation, there are usually a large number of weak lines for which the calculated line strengths can deviate from the true values by orders of magnitude. For weak lines, experimental measurements greatly suffer from many factors, such as the uncertainty of the base line in the determination of the intensities. Thus, for both theory and experiment, statistical distributions of the values are far from normal. For the logarithms of line strengths and

intensities, statistical distributions of the values are much closer to normal.

III.B. Matching Different Theoretical Calculations with Each Other

Another property that is a good identifier of a quantum state is the eigenvector. In quantum mechanical calculations of line strengths, the amplitudes of the eigenvector components are the main contributing factors. Thus, it is natural to use eigenvectors to identify atomic states in theoretical models.

To calculate different atomic properties, it is usually necessary to use different theoretical approaches. For example, to accurately predict the energy levels, the best approach is often the LSF with Cowan's codes.¹⁷ However, the approximations used in these codes lead to large errors in calculations of transition probabilities. Therefore, the latter quantities are usually obtained with much better accuracy using more sophisticated methods such as MBPT, multiconfiguration Hartree-Fock, MCDF, or RCI. Thus, it is often necessary to merge together results of calculations that use very different atomic models. This poses a task of establishing the correspondence between the eigenvectors produced by different models. It is not always possible to establish such correspondence in a unique and meaningful way, because the approximations of the models may be too different. However, a partial correspondence usually exists and can be established. The method for this, used in my version of Cowan's LSF code RCE,¹⁷ is based on calculating the distance between the eigenvectors in the multidimensional space of the basis set. In the LSF, each iteration produces a different set of values for the Slater parameters, which means that the atomic model changes. This requires establishing a correspondence between the eigenvectors obtained before and after each iteration. My method is illustrated in Fig. 7.

Suppose we have two sets of eigenvectors V_i and V'_j produced by two close models in the same set of basis states. Each of V_i and V'_j are defined by the set of their projections on the axis, which are the amplitudes of the corresponding basis states in the vector. The task is to decide which index i corresponds to each j . To do that, we calculate the squared distances $d_{ij}^2 = \sum (V_{ik} - V'_{jk})^2$, where V_{ik} and V'_{jk} are the amplitudes of basis state k in the two eigenvectors, and the summation is over all basis states. The best choice of correspondence between the two sets of eigenvectors should minimize the sum of all d_{ij}^2 . In general, for an arbitrarily large size N of the basis set, a brute force solution of such a minimization problem by considering every possible combination (i, j) is technically impossible, because it would involve an exponentially large number of operations, on the order of N^N . However, in practice we can quickly find a reasonably good solution, assuming that the two models are not too far from each other. We start by considering only the relatively pure eigenvectors, i.e.,

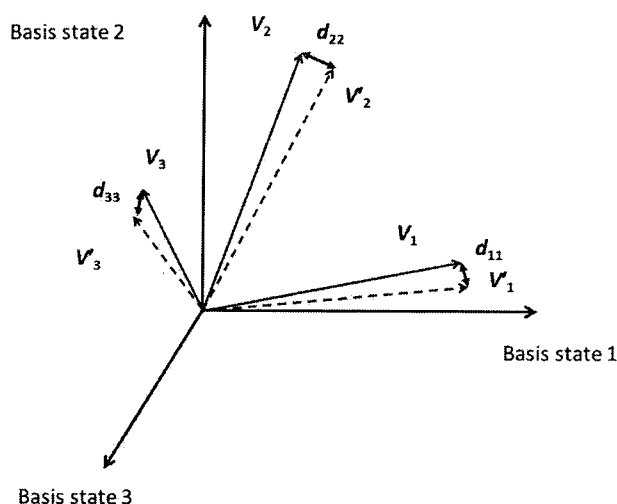


Fig. 7. Establishing correspondence between two sets of eigenvectors V_i (blue solid lines) and V'_j (red dashed lines) produced by two close theoretical atomic models. The correspondence is established by minimizing the sum of squares of distances d_{ij} (green double-headed arrows) between each pair of eigenvectors (see text).

those that have $>50\%$ contribution of one basis state. Establishing correspondence between these pure eigenvectors is easy and straightforward. Eliminating these pure eigenvectors effectively reduces the size N of the problem. Then we proceed with each of the highly mixed eigenvectors V'_j by finding the closest of the remaining unassigned V_i , i.e., the one that minimizes the squared distance d_{ij}^2 . Once the closest match is found, V_i and V'_j are removed from the unassigned set, again reducing the size of the remaining problem. This step is repeated until all eigenvectors V'_j are uniquely assigned to V_i . The algorithm actually implemented in my version of RCE¹⁷ is somewhat more complicated. For example, it accounts for a possible change of sign of all components of V'_j after the LSF iteration.

As noted above, comparing the eigenvectors is physically meaningful, because the amplitudes of the eigenvector components are the quantities determining the observable properties of quantum states, such as radiative and collisional rates and Landé factors. For human observers, these properties, along with the excitation energy and the J value, are the characteristics that constitute the identity of a quantum state.

The procedure described above can easily be extended for the case when the two basis sets have different dimensions. Then only a subset of the smallest dimension is used to identify the eigenvectors.

III.C. Selecting the Best Values for Transition Probabilities

Wiese³² discussed several crucial factors for estimating the validity of calculated transition probabilities, such

as consideration of configuration interaction, near coincidences of energy levels, cancellation effects, relativistic corrections, and convergence of results and of the dipole length and velocity forms. For experimental measurements, he discussed such crucial factors as the validity of the plasma model, absence or good account of self-absorption, and accuracy of intensity calibration. For lifetime measurements, important factors are selective excitation, proper account of collisional effects and radiation trapping, absence of line blending, and, for some types of experiments, account of polarization effects and quantum beats. Once the available data are checked for these crucial factors and unreliable data are eliminated, it is not uncommon to be left with several partially overlapping sets of data, from which the best ones have to be chosen, and their uncertainties have to be assessed.

In my practice, I have found the following procedure to be very productive: One starts with selecting the best available experimental data with well-defined uncertainties. For example, if available, one should use experimental A values derived from spectrally calibrated measurements of branching fractions normalized to the absolute scale by using well-measured radiative lifetimes. This set of data should be used for comparisons with other, less-reliable data sets. When comparing calculated A values with the reference data, one should differentiate the data by the line strength. It is commonly observed that both calculations and measurements are much more accurate for strong lines than for weak ones. Thus, it is usually possible to select a threshold value for the line strength below which the calculations are totally unreliable (have uncertainties on the order of orders of magnitude) and to find certain ranges of line strengths for which the uncertainty of the calculations can be reasonably estimated by deviations from the reference values. These ranges of line strengths are different for each method of calculation and for each atomic spectrum. Once the uncertainties are estimated for the limited set of compared values, they can be extrapolated to other data within the same range of line strengths from the same calculation. If the uncertainties are small enough, these data can be included in the reference set and used for estimating the remaining data sets. The final selection should be based on the choice of data having the smallest estimated uncertainties.

The above procedure is illustrated in Fig. 8 for the case of Cowan code calculations for Ag II.¹³ The shaded region of extremely weak transitions is unusable because of too large uncertainties of the calculation.

It is not uncommon to have a need to recalibrate some previously published results using more recent reference data than available to the original authors. For example, Ferrero et al.³⁷ calibrated their measurements of radiative branching fractions in Ag II by their own single-configuration Hartree-Fock calculations of lifetimes, which they assumed to be accurate within 5%. Later, beam-laser measurements of lifetimes by Biémont

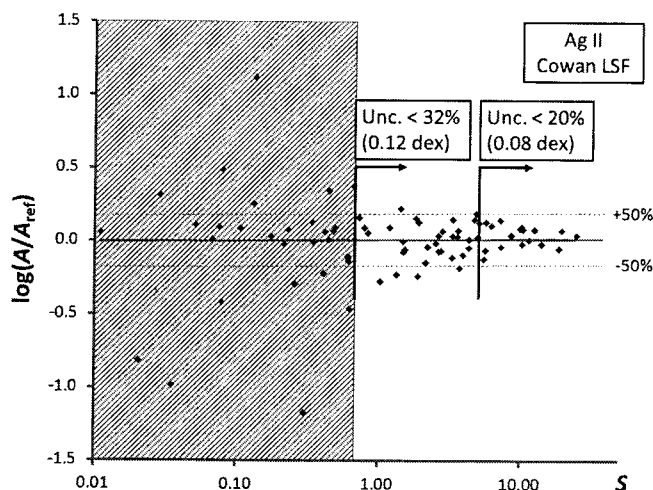


Fig. 8. Selection of A values based on line strength S .

et al.³⁸ proved that this estimate was far too optimistic. However, the measurements of Ferrero et al.³⁷ still can be used to obtain accurate A values, if they are recalibrated with experimental lifetimes from Biémont et al.³⁸

III.D. Checking for Regularities

It is often possible to spot errors in transition probability data by checking for known regularities along line series or along isoelectronic sequences. For example, as noted in Ref. 33, transition probabilities given by Froese Fischer et al.³⁹ for high members of the $2p^63p-2p^6ns$ and nd series of neutral sodium are incorrect. This is easily revealed by looking at the trend of the A values along the series. In such simple single-electron spectra with no significant perturbations, transition probabilities in a Rydberg series of lines should monotonically decrease with increasing principal quantum number. The data of Ref. 39 do not follow this trend.

IV. ERROR CHECKING

The last step before inserting the critically evaluated data into a reference database is the error checking. Although the journal publishing process already involves extensive error checking, the requirements for database error checking are essentially different. For example, published papers on atomic spectroscopy often use some shortened notation for energy levels in order to save space. In the database, the notation should be expanded to conform to general standards that can be easily formulated for all spectra so that there should be no need to make special notes for each spectrum. Many procedures, such as the verification of the correspondence between the labels used in the level and line tables, uniqueness of the

level names used, and their conformity to conventions used in similar spectra, are easier to implement with a database than with document-based software. Very often, at the stage of inserting data into the database, many misprints missed in the publication process are revealed. If a database is intended to store several million data pieces, having erroneous data imposes severe maintenance problems. Correcting one small error in the database can easily take half an hour of labor, because changing one datum may require additional consistency checking and should be documented. I estimate that an error rate acceptable for such large databases is $<0.01\%$. If there are more errors, their correction would require unacceptably large amounts of maintenance work.

In addition to the data checking points mentioned above, it is necessary to verify the correctness of vacuum-to-air conversion for wavelengths,^a correspondence of wavelengths to wave numbers, correspondence of A values to the oscillator and line strengths for each type of transition ($E1$, $M1$, $E2$, etc.), and correctness of bibliographic references. Different databases may require different error checking, depending on their structure and contents.

V. CONCLUSIONS

This paper summarizes current methods of critical evaluation of wavelengths, energy levels, and transition probabilities for atoms and atomic ions at NIST. The general workflow and basic steps of critical evaluation of such data are described, and several practical examples are given.

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^aThe convention used in critically evaluated spectral line lists published by NIST is to give the wavelengths between 2000 and 20,000 Å in standard air, which is defined as dry air containing 0.033% of CO_2 at a pressure of 101.325 kPa and a temperature of 15°C. Conversion from vacuum to air wavelengths and vice versa is made with the five-parameter formula from Peck and Reeder.⁴⁰

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