

A Procedure to Obtain the Effective Nuclear Charge from the Atomic Spectrum of Sodium

O. Sala,* K. Araki, and L. K. Noda

Instituto de Química, Universidade de São Paulo, C.P. 26077, 05599-970, São Paulo, Brazil; *oswsala@quim.iq.usp.br

Experiments involving the spectrum of atomic hydrogen are very useful for introducing the quantization of energy levels (1–3) to chemistry students. Using the Balmer series (4, 5), it turns out that the energy of the lone orbiting electron depends exclusively on the principal quantum number, n . In this case the electron is solely subject to the electrostatic influence of the nucleus. The sodium atom, as any alkali metal, resembles the hydrogen atom in having only one electron in the valence shell. However, the interelectronic interactions must be considered in the energy calculations because of the penetration of this electron into the inner closed shells. As a consequence of the radial probability-density distribution (Fig. 1) the energy levels depend not just on the principal quantum number, but also on the angular momentum quantum number, l . A quantity called the quantum defect, μ , which accounts for the distinct capability of the valence electrons to penetrate into the atom's inner closed shells, is usually introduced (5).¹

On the other hand, many concepts on atomic structure (energy levels, ionization potentials, electronegativity of the elements, and so on) are discussed in terms of effective nuclear charges. In the case of the valence electron of an alkali metal this quantity involves the shielding effect of the inner-shell electrons on the nuclear charge Z^* (6–10). The effective nuclear charge depends on n and l quantum numbers, and can be used to describe the spectral series. It seems to be an easier concept for students to understand than the quantum defect, because it retains the meaning of an integer quantum number, as learned in basic courses. These advantages in using Z^* instead of μ , together with the method presented in this article, overcome the advantage that μ is practically constant for a given l (only one value of μ has to be calculated for each angular momentum, from the experimental data).

We describe a simple graphical method for using spectral data to determine the effective nuclear charges, Z_{nl}^* , felt by the valence electron of sodium in the ground and various excited energy states, the shielding constants σ_{nl} , and the energy levels. The shielding constant represents the amount of nuclear charge screened by the inner electrons on the outer

n/l electron, $\sigma_{nl} = Z - Z_{nl}^*$, where Z is the total nuclear charge. This procedure has been used in our undergraduate physical chemistry laboratory classes. Its accuracy is high enough for didactic purposes.

This experiment is very convenient for introducing the concept of angular momentum and its effect on the energies of the orbitals, as well as the concepts of a main subject like spectroscopy.

Methods

The energy term for the sodium atom, $T_{nl} = R(1/(n - \mu)^2)$, corresponds to the binding energy (cm^{-1}) of an electron in an n/l orbital. Introducing the effective nuclear charge the expression becomes $T_{nl} = R(Z_{nl}^*)^2/n^2$. Therefore the Rydberg series (4) for the sodium atom may be rewritten as:

$$\text{Sharp series } \nu_s = R \left[\frac{(Z_{3p}^*)^2}{3^2} - \frac{(Z_{ns}^*)^2}{n^2} \right] \quad n = 4, 5, 6, \dots \quad (1)$$

$$\text{Principal series } \nu_p = R \left[\frac{(Z_{3s}^*)^2}{3^2} - \frac{(Z_{np}^*)^2}{n^2} \right] \quad n = 3, 4, 5, \dots \quad (2)$$

$$\text{Diffuse series } \nu_d = R \left[\frac{(Z_{3p}^*)^2}{3^2} - \frac{(Z_{nd}^*)^2}{n^2} \right] \quad n = 3, 4, 5, \dots \quad (3)$$

where ν_l are the wavenumbers (cm^{-1}) corresponding to the transitions between the two terms in the second member.

The effective nuclear charge is a measure of the average nuclear charge felt by the outermost electron in the various orbitals, considering the interelectronic repulsions and its penetration capability. Therefore, effective nuclear charges can be evaluated from experimental data using the eqs 1 to 3. Instead of solving these equations analytically, a graphical approach using spreadsheet software (Origin, Excel, etc.) was employed.

Experimental Procedure

The sodium spectrum can be obtained with any kind of spectrometer, from an old photographic instrument to a modern recording spectrophotometer. The spectrum shown in Figure 2 was obtained with a Jobin Yvon U-1000 instrument that gives the spectrum directly in cm^{-1} . Owing to the exponential variation of the line intensities in a spectral series, the spectrum in the high-energy side was plotted on a logarithmic scale. In the 16,000–18,500 cm^{-1} region the height of the lines is the intensity (nonlogarithmic) after passing

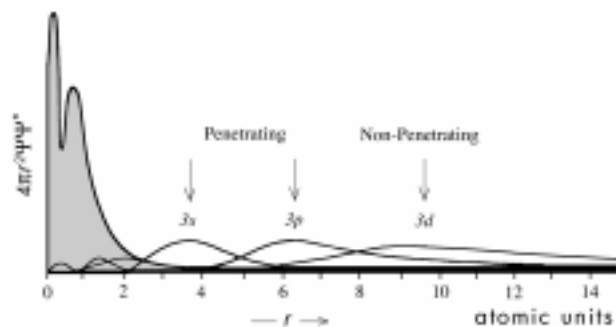


Figure 1. Radial probability-density distribution (distance in atomic units) for the 3s, 3p, and 3d electrons in the sodium atom. The shaded area corresponds to the core.

through a Corning glass filter #512 (or a neodymium salt solution); this filter reduces drastically the intensity of the yellow line, indicated by (p). The spectrum can be obtained in about half an hour. The calculations and interpretation of the results may take about four hours. The baseline in the high-frequency side shows a structure due to rotational-vibrational bands of Na_2 molecules. This will not be discussed because it is beyond the scope of this article.

Identification of the Spectral Series

The first step in analyzing the emission spectrum is to correctly attribute the spectral series. By a close inspection of the spectrum (Fig. 2), disregarding the fine structure (only the transitions involving the $3P_{3/2}$ level, in the doublets, will be considered in the following), it is possible to distinguish two progressions of lines, indicated by (a) and (b), which become closer and closer going to higher wavenumbers. Considering eqs 1 to 3, it is evident that when $n \rightarrow \infty$ the sharp and diffuse series tend to the same limit, $T_{3p} = R(Z_{3p}^*)^2/3^2$. Therefore, the two progressions can be attributed to these series.

Assignment of Diffuse Series

The equation for the diffuse series, eq 3, can be written as $\nu_d = A - BX$, where $X = 1/n^2$, $B = R(Z_{nd}^*)^2$. From a plot of the wavenumbers (cm^{-1}) as a function of $1/n^2$ for the (a) and (b) progressions only the diffuse series should give a straight line because the d electron is almost nonpenetrating and Z_{nd}^* can be assumed as 1. The correct attribution of the principal quantum numbers to the lines can be determined by trial and error, assigning different n values to the first line in the spectrum (starting with $n = 3$) until the best correlation coefficient is obtained from a linear regression. In this way, the diffuse series can be identified as the progression (a) in Figure 2 and the Rydberg constant and the value of T_{3p} can be obtained, respectively, from the slope (B) and the linear coefficient (A) of this straight line. We obtained $R = 110,562 \text{ cm}^{-1}$ (lit. $109,734 \text{ cm}^{-1}$ [5]) and $T_{3p} = 24,489 \text{ cm}^{-1}$ (lit. $24,476 \text{ cm}^{-1}$ [11]), as shown in Figure 3.

Assignment of Sharp Series and Calculation of Z_{ns}^*

The values of $(Z_{ns}^*)^2$ for the ns levels can be determined by substituting the appropriate ν_s (beginning with the first of the (b) lines in Fig. 2) and n values into the expression $(Z_{ns}^*)^2 = (T_{3p} - \nu_s)n^2/R$ ($T_{3p} = 24,489 \text{ cm}^{-1}$ and $R = 110,562 \text{ cm}^{-1}$ were previously determined).

The correct attribution of n to the ν_s (with $n \geq 4$) can be obtained calculating the energy terms ($T_{ns} = R(Z_{ns}^*)^2/n^2$) from the $(Z_{ns}^*)^2$ above, for $n = 4, 5, 6, \dots$, for $n = 5, 6, 7, \dots$ and for $n = 6, 7, 8, \dots$. It is observed that only the set of values starting with $n = 5$ gives the correct values of the energy terms by comparison with the values from the literature (11).

It is useful to find an expression correlating $(Z_{ns}^*)^2$ with any value of the principal quantum number, because it allows the prediction of the spectral lines even for those transitions out of the observed spectral region. As the effective nuclear charge is expected to decrease with increasing n for a fixed l , plots of $(Z_{ns}^*)^2$ versus $1/n$ and $1/n^2$ were tried. The plot as a function of $1/n^2$ (Fig. 4(a)) shows a linear dependence, fitted by the linear regression

$$(Z_{ns}^*)^2 = 17.695/n^2 + 1.162 \quad (4)$$

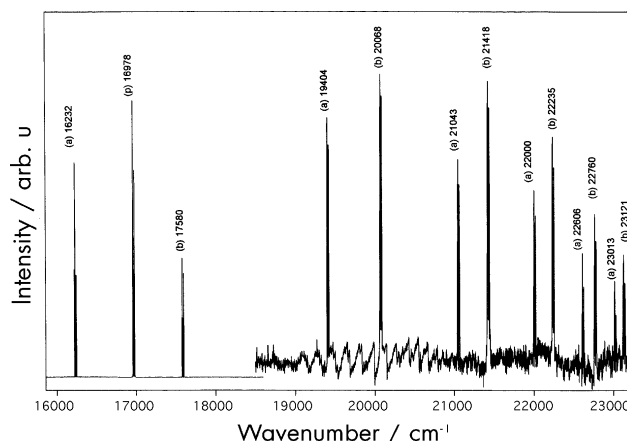


Figure 2. Emission spectrum of the sodium atom, intensity in arbitrary units. In the 16,000–18,500 cm^{-1} region a didymium No. 512 filter (Corning) was employed to decrease the intensity of the yellow line (p). In the high-energy side, a logarithmic scale was used because of the enormous difference in the intensities of the lines.

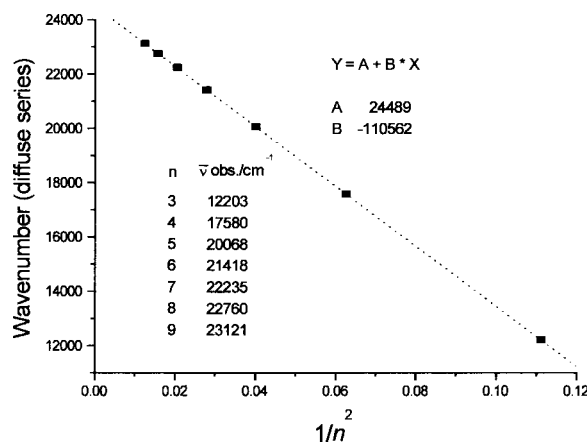


Figure 3. Plot of experimental wavenumbers for the diffuse series as a function of $1/n^2$ (filled squares) and the corresponding linear regression (dotted line).

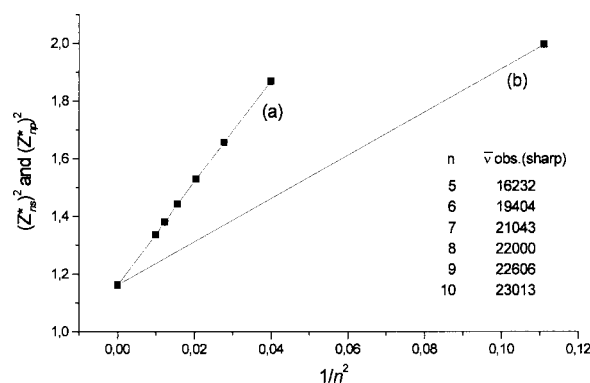


Figure 4. (a): Plot of $(Z_{ns}^*)^2$ as a function of $1/n^2$ with the $(Z_{ns}^*)^2$ calculated from the spectral values of the sharp series (filled squares) and the corresponding linear regression (full line; eq 2). (b): Plot of $(Z_{np}^*)^2$ as a function of $1/n^2$ for the principal series (filled squares) and the corresponding linear regression (full line; eq 3).

From this equation the squared effective nuclear charge can be estimated for any value of $n \geq 4$ (see Table 1). The T_{3s} and $(Z_{3s}^*)^2$ values can be determined straightforwardly from the first line of the principal series (yellow line); since T_{3p} is already known and $T_{3s} - T_{3p} = 16,978 \text{ cm}^{-1}$, we have $(Z_{3s}^*)^2 = 41,467 \times 3^2/R$.

Calculation of Z_{np}^* and the Energy Terms

Unfortunately, only the 3S–3P transition of the principal series is observed in the visible region of the spectrum (indicated by (p) in Fig. 2). The remaining transitions have lines in the ultraviolet region and are filtered by the glass tube of the sodium lamp. Even so, it is possible to find the relationship for the $(Z_{np}^*)^2$ because as $1/n^2$ tends to zero, $(Z_{np}^*)^2$ and $(Z_{ns}^*)^2$ converge to the same limit; that is, when $n \rightarrow \infty$, $(Z_{\infty p}^*)^2 = (Z_{\infty s}^*)^2 = 1.162$, the linear coefficient of eq 4. The value of $(Z_{3p}^*)^2$ can be calculated from the term T_{3p} , $(Z_{3p}^*)^2 = 24,488 \times 3^2/R = 1.9935$. These two points define a straight line (Fig. 4(b)) described by the equation

$$(Z_{np}^*)^2 = 7.482/n^2 + 1.162 \quad (5)$$

This equation can be used to evaluate the squared effective nuclear charges of the np electrons for $n \geq 3$. From these values it is possible to calculate the energies of the transitions in the ultraviolet region. The validity of eq 5 can be verified by comparison with the energy levels from the literature (11).

The calculated effective charges and their squared values are listed in Table 1, showing their dependence on the angular momentum and principal quantum numbers. As expected, the values of the calculated effective nuclear charges follow the sequence

$$Z_{ns}^* > Z_{np}^* > Z_{nd}^*$$

To verify the reliability of this new procedure, the energies of the ns , np , and nd electrons ($3 \leq n \leq 10$) were calculated, according to $T_{nl} = R(Z_{nl}^*)^2/n^2$, and compared with the values from the literature (Table 2). The errors are reasonably low and of the same magnitude as those obtained using the method of quantum defects (12).

The shielding factor σ_{nl} can be calculated from the expression $(Z - \sigma_{nl}) = Z_{nl}^*$ (Z = atomic number). Its values are presented in Table 1 for the ns and np levels. As expected, σ_{nl} is a function of the quantum numbers n and l , because the ability of the valence electron to penetrate into the closed shells depends on the level in which it is found.

In conclusion, our method makes it possible to determine experimentally the effective nuclear charges, the shielding factors, and the energies of the several states of the valence electron of the sodium atom with good accuracy. The most important point is that this charge can be considered as responsible for the effect of the interelectronic interactions without changing the integer value of the quantum number in the denominator in the Rydberg equations.

Table 1. Calculated Effective Nuclear Charges and Shielding Factors for the Sodium Valence Electron

n	Sharp Series			Principal Series			Diffuse Series	
	$(Z_{ns}^*)^2$	Z_{ns}^*	σ_{ns}	$(Z_{np}^*)^2$	Z_{np}^*	σ_{np}	$(Z_{nd}^*)^2$	Z_{nd}^*
3	3.3755	1.84	9.16	1.9898	1.41	9.59	1.0000	1.00
4	2.2681	1.51	9.49	1.6271	1.27	9.73	1.0000	1.00
5	1.8699	1.37	9.63	1.4601	1.21	9.79	1.0000	1.00
6	1.6537	1.28	9.72	1.3691	1.17	9.83	1.0000	1.00
7	1.5233	1.23	9.77	1.3142	1.15	9.85	1.0000	1.00
8	1.4387	1.17	9.83	1.2786	1.13	9.87	1.0000	1.00
9	1.3806	1.16	9.84	1.2541	1.12	9.88	1.0000	1.00
10	1.3391	1.14	9.86	1.2367	1.11	9.89	1.0000	1.00

Note

1. The quantum defect is a function of the angular momentum quantum number and is practically independent of the principal quantum number. Using the Rydberg series (12, 13) the quantum defects can be determined from the linear and angular coefficients in the plot of the wavenumbers of the spectral lines versus $1/n^2$, starting from the diffuse series where the μ for d orbitals (nonpenetrating orbit) is nearly equal to zero. Then, the energy terms $T_{nl} = R/(n - \mu)^2$, where R is the Rydberg constant, can be estimated by substituting the appropriate values of μ and n into this expression.

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Table 2. Calculated Energy Terms and Literature Values for the Sodium Atom

n	T_{ns}/cm^{-1}			T_{np}/cm^{-1}			T_{nd}/cm^{-1}		
	calcd	ref 11	δ (%) ^a	calcd	ref 11	δ (%) ^a	calcd	ref 11	δ (%) ^a
3	41,467	41,450	0.04	24,443	24,476	0.13	12,285	12,277	0.06
4	15,673	15,710	0.23	11,248	11,177	0.63	6,910	6,901	0.15
5	8,270	8,249	0.25	6,457	6,407	0.78	4,422	4,413	0.20
6	5,079	5,077	0.04	4,205	4,152	1.27	3,071	3,062	0.29
7	3,437	3,438	0.03	2,965	2,908	1.97	2,256	2,249	0.31
8	2,486	2,481	0.20	2,208	2,151	2.65	1,727	1,721	0.41
9	1,885	1,875	0.51	1,711	1,655	3.38	1,365	1,359	0.44
10	1,480	1,467	0.92	1,367	1,312	4.19	1,106	1,100	0.54

^aRelative error.