

## On the Computation of Combination Differences for the Analysis of Molecular Diatomic Spectra

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A fast method to calculate combination differences, related to the rotational analyses of diatomic molecular spectra is presented. The computational method uses a linear fitting of all possible differences between lines of R- and P- type branches. The time-consuming search for coincidences is reduced to compare slopes of the linear fitting. An actual example is given for the  $\text{La}^{16}\text{O}$  spectrum.

Apresenta-se um método rápido para o cálculo de diferença combinadas, relacionadas a análise dos espectros das moléculas diatômicas. O método computacional usa um ajuste linear de todas as possíveis diferenças entre as linhas dos ramos de tipo R e de tipo P. A procura de coincidências, que consome muito tempo, é reduzida à comparação das inclinações do ajuste linear. Um exemplo concreto é fornecido pelo espectro da  $\text{La}^{16}\text{O}$ .

Several are the steps to go through in the analysis of molecular diatomic spectra. After the plate has been measured, the screw-readings have to be reduced to wavelengths and wavenumbers. This can be accomplished by fitting the position of the standard lines to a high degree polynomial and the coefficients obtained can be used to calculate the wavelengths and wavenumbers of the unknown lines. Next, the picking out of branches has to be done<sup>1-3</sup> and then a rotational quantum number must be assigned to each line of every branch. This assignment is one of the leading steps to derive the rotational constants of the molecule. But, unless the origin is resolved, which is not the usual case, it is previously necessary to find the so-called *combination differences*<sup>4</sup>. This task can be tedious enough and very time consuming, unless some combination differences are already known from previous analysis connected to the level under analysis. Otherwise, a computer technique, as the one to be described, will be preferable.

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The relations<sup>4</sup>

$$\Delta_2 F'(J) = R(J) - P(J) = 4B'_v \left( J + \frac{1}{2} \right), \quad (1)$$

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = 4B'_v \left( J + \frac{1}{2} \right), \quad (2)$$

are called combination differences for the R and P branches. The notation is the usual one in molecular spectroscopy. We are not taken into account  $D_v$  constants in Eqs. (1) and (2) because they are not important in our discussion, i.e. assignment of  $J$  values.

Without knowing  $J$ , we have to use a relative numbering of the lines in every branch we have picked out, say  $x$ , which is related to  $J$  simply by:  $J = x + p$ , where  $p$  is a constant to be determined. All possible differences between R and P branches should be performed in at least two bands with a common level (lower common vibrational level to compute Eq. 1, and upper one to compute Eq. 2).

Every time we match an R with a P branch, we obtain a set of combination differences. Besides, we have to search for the right one in each band.

Now, the relationships 1 and 2 can be written as

$$\Delta_2 F(x) = Ax + C, \quad (3)$$

where the coefficients  $A$  and  $C$  will let us know  $B'_v$  and  $p$ , and then  $J$  will be easily found.

To compute the coefficients  $A$  and  $C$  we fit each set of combination differences to the linear equation (3), using a least-squares fit technique. So, we obtain as many  $A$  and  $C$  values as the number of combination differences we can form in each band.

To form the combination differences in each band we proceed as follows: if we label as  $R_i$  and  $P_i$  every line of the R and P branches, we can have this first set:  $R_1 - P_1, R_2 - P_2, \dots, R_k - P_k$ . Since the number of lines in each branch is not necessarily the same, these differences will be performed as long as both branches can be matched.

If we now shift the R branch with respect to the P branch, we will have this new set:  $R_1 - P_2, R_2 - P_3, \dots, R_k - P_{k+1}$ . We proceed in this way until all the differences are formed.

After finishing the above operation in at least two bands, and the linear fitting is performed, we have to search for coincidences between one slope

(*A*'s values) of the first band with one of the second one. When the coincidence is found, we can see that the corresponding sets have members that are, within experimental error of measurements, the same. Using the unique value of *A* found in this way, we obtain *B*., for the upper or lower level we are dealing with. The coefficient *C* will be different, unless, which is a rare case, we are using branches with lines covering the same range of *J* values. In every band, *C* will allow us to determine the *J* value of the first member of the set of combination differences. Since the linear fitting will be affected for some error, *J* will not be found as an integer or a half integer (depending of the type of electronic transition), but will be so close to it that we can round it without uncertainty.

After knowing *J* for the first member of the set, the associated *R*, and *P*, lines can be easily numbered, and then all the other lines of the branches we are using.

It may occur that the first line in the *R* branch we have picked up has a lower *J* value than the first one in the *P* branch. In such a case, no coincidence between sets of combination differences will be found at all. But we can reverse the role of *R* and *P* conveniently, to proceed as before. The only change will be the negative slopes in both bands, but the entire procedure remains the same.

We have written the above procedure in a Fortran language that proved to be very satisfactory. The time consuming search for combination differences is reduced to compare two sets of slopes, what is rapidly done because they are printed out in increasing or decreasing order for each band. Any risk of close coincidence by chance is avoided because all possible differences are taken into account.

We have been using this technique to make a detailed revision of the analysis of  $\text{La } ^{16}\text{O}$  and to analyse  $\text{La } ^{18}\text{O}$  with excellent results. In Table I we show excerpts of branches actually used in our work. They are the *R* and *P* branches of the *O-O* band of the *B-X* system of  $\text{La } ^{16}\text{O}$  and the *R*- and *P*-type (here the analysis is more involved, and is not within the scope of this paper) of the *O-O* band in the region of 7,900 Å of the *A-X* system. The data given are our own measurements using a semi-automatic photoelectric comparator and thorium lines excited in electrodeless discharge as standard references.

Table II shows excerpts of the computer output. The first three sets of differences belong to the *B-X* system and the last three to the *A-X* system.

J	R (J)	INT.	P (J)	INT.	J	R (J)	INT.	P (J)	INT.
1	0.000	0.	0.000	0.	1	0.000	0.	0.000	0.
2	0.000	0.	0.000	0.	2	0.000	0.	0.000	0.
3	0.000	0.	0.000	0.	3	0.000	0.	12635.280	92.
4	0.000	0.	0.000	0.	4	0.000	0.	12635.015	79.
5	0.000	0.	0.000	0.	5	0.000	0.	12634.729	76.
6	0.000	0.	0.000	0.	6	0.000	0.	12634.441	72.
7	0.000	0.	0.000	0.	7	12645.490	48.	12634.160	74.
8	0.000	0.	0.000	0.	8	12646.560	42.	12633.845	77.
9	0.000	0.	0.000	0.	9	12647.650	49.	12633.532	72.
10	0.000	0.	0.000	0.	10	12648.680	55.	12633.207	69.
11	0.000	0.	0.000	0.	11	12649.700	52.	12632.862	85.
12	0.000	0.	0.000	0.	12	12650.720	53.	12632.498	85.
13	0.000	0.	0.000	0.	13	12651.740	56.	12632.132	90.
14	0.000	0.	0.000	0.	14	12652.720	56.	12631.756	85.
15	0.000	0.	0.000	0.	15	12653.700	63.	12631.353	79.
16	0.000	0.	0.000	0.	16	12654.690	61.	12630.949	80.
17	0.000	0.	0.000	0.	17	12655.640	57.	12630.527	80.
18	0.000	0.	0.000	0.	18	12656.590	62.	12630.089	81.
19	0.000	0.	0.000	0.	19	12657.530	63.	12629.634	83.
20	0.000	0.	0.000	0.	20	12658.450	66.	12629.174	83.
21	0.000	0.	0.000	0.	21	12659.370	68.	12628.706	83.
22	0.000	0.	0.000	0.	22	12660.290	72.	12628.225	82.
23	0.000	0.	0.000	0.	23	12661.160	64.	12627.734	81.
24	0.000	0.	0.000	0.	24	12662.030	74.	12627.220	82.
25	0.000	0.	0.000	0.	25	12662.910	74.	12626.714	82.
26	0.000	0.	0.000	0.	26	12663.750	68.	12626.182	82.
27	0.000	0.	17815.149	89.	27	12664.590	80.	12625.633	82.
28	0.000	0.	17813.776	107.	28	12665.430	82.	12625.083	82.
29	0.000	0.	17812.511	121.	29	12666.260	81.	12624.510	82.
30	17843.872	179.	17811.115	133.	30	12667.050	87.	12623.930	82.
31	17843.687	178.	17809.777	155.	31	12667.850	71.	12623.330	82.
32	17843.520	179.	17808.428	140.	32	12668.640	72.	12622.730	104.
33	17843.322	179.	17806.979	93.	33	12669.400	80.	12622.106	106.
34	17843.072	176.	17805.506	102.	34	12670.140	95.	12621.500	85.
35	17842.829	175.	17804.074	143.	35	12670.890	96.	12620.900	78.
36	17842.573	170.	17802.623	113.	36	12671.634	92.	12620.261	71.
37	17842.271	173.	17801.077	114.	37	12672.358	104.	12619.607	75.
38	17841.984	174.	17799.511	131.	38	12673.068	104.	12618.947	75.
39	17841.620	168.	17798.000	138.	39	12673.765	102.	12618.269	79.
40	17841.275	174	17796.440	109.	40	12674.466	104.	12617.580	75.
41	17840.884	170.	17794.834	125.	41	12675.148	114.	12616.878	84.
42	17840.495	175.	17793.178	116.	42	12675.798	109.	12616.166	76.
43	17840.048	172.	17791.551	97.	43	12676.438	112.	12615.444	77.
44	17839.586	168.	17789.890	94.	44	12677.113	112.	12614.713	87.
45	17839.098	166.	17788.200	94.	45	12677.709	126.	12613.962	91.
46	17838.580	166.	17786.488	93.	46	12678.322	127.	12613.199	80.
47	17838.076	169.	17784.751	94.	47	12678.918	130.	12612.415	81.
48	17837.519	158.	17782.958	113.	48	12679.489	123.	12611.629	81.
49	17836.937	155.	17781.205	147.	49	12680.041	119.	12610.806	82.
50	17836.361	167.	17779.459	133.	50	12680.590	120.	12610.014	82.
51	17835.737	151.	17777.594	107.	51	12681.118	150.	12609.204	82.
52	17835.082	157.	17775.737	114.	52	12681.649	142.	12608.367	0.
53	17834.428	155.	17773.848	136.	53	12682.159	145.	12607.533	0.
54	17833.724	152.	17771.979	142.	54	12682.657	140.	12606.692	81.

**Table I** - Excerpt of wavenumbers and relative intensities of lines of R- and P-type branches of  $\text{La}^{16}\text{O}$  Left side of page corresponds to the 0-0 band at 5,600 Å of the B-X system The right side to the O-O sub-band at 7,877 Å of the A-X system

At the beginning of each set, x indicates that a certain line of the second branch has been matched with the first line of the first branch to start the set of differences. A and C have the meaning given before. Next, the standard deviation of the recalculated differences is given, and finally, the J number corresponding to the first difference in the set.

x= 11	A= 1.3711	C= 41.42	STAND. DEV. = .023	FIRST J = 30.70												
42.79	44.17	45.52	46.88	48.23	49.65	51.02	52.38	53.78	55.13	56.52	57.92	59.29	60.58	61.99	63.36	64.73
66.09	67.43	68.83														
x= 12	A= 1.3943	C= 42.92	STAND. DEV. = .023	FIRST J = 31.28												
44.36	45.68	47.08	48.48	49.89	51.27	52.68	54.07	55.49	56.86	58.31	59.67	61.03	62.45	63.84	65.25	66.60
67.99	69.42															
x= 13	A= 1.4180	C= 44.44	STAND. DEV. = .025	FIRST J = 31.84												
45.87	47.24	48.68	50.14	51.52	52.93	54.37	55.78	57.23	58.66	60.07	61.42	62.90	64.31	65.73	67.11	68.49
69.97																
x= 6	A= 1.3874	C= 10.33	STAND. DEV. = .073	FIRST J = 7.94												
11.64	13.02	14.44	15.81	17.20	18.58	19.98	21.36	22.75	24.16	25.55	26.95	28.35	29.74	31.14	32.55	33.94
35.31	36.72	38.11	39.50	40.92	42.33	43.72	45.12	46.53	47.90	49.24	50.62	52.02	53.41	54.79	56.18	57.58
58.98	60.35	61.72	63.15	64.51	65.90	67.28	68.68	70.02	71.38	72.75	74.11	75.46	76.85	78.23	79.58	80.99
82.36	83.73	85.09														
x= 7	A= 1.3992	C= 10.64	STAND. DEV. = .074	FIRST J = 8.11												
11.95	13.35	14.78	16.18	17.56	18.96	20.38	21.77	23.17	24.60	26.00	27.41	28.82	30.22	31.63	33.07	34.44
35.84	37.27	38.66	40.08	41.50	42.93	44.32	45.74	47.14	48.50	49.87	51.28	52.68	54.08	55.48	56.88	58.30
59.70	61.08	62.47	63.91	65.29	66.69	68.11	69.47	70.83	72.22	73.58	74.95	76.35	77.75	79.12	80.48	81.91
83.28	84.66	86.04														
x= 8	A= 1.4110	C= 10.97	STAND. DEV. = .074	FIRST J = 8.27												
12.28	13.69	15.15	16.54	17.94	19.36	20.79	22.19	23.61	25.05	26.46	27.88	29.30	30.71	32.15	33.57	34.97
36.39	37.82	39.24	40.66	42.10	43.53	44.94	46.35	47.74	49.13	50.53	51.94	53.36	54.77	56.19	57.59	59.02
60.43	61.83	63.23	64.69	66.08	67.51	68.90	70.28	71.67	73.05	74.42	75.84	77.25	78.64	80.02	81.40	82.83
84.21	85.61	87.01														

**Table II**- Excerpt of the print-out of combination differences for branches given in Table I. The first three sets correspond to the B-X system. The others to the A-X system. Coincidence is found for sets with  $x = 12$  and  $x = 7$ . The number of elements in each of these sets are different due to different range of  $J$  covered by the branches.

The coincidence searched for has been found between the second sets in each band. If we think that  $A = 1.4180$ , and  $A = 1.4110$  are also close enough, an inspection of the corresponding differences will convince us that they do not agree at all. Sometime this check should be done, but it is almost no effort to compare just a few slopes, taking into account that for the example given, 30 sets of combination differences have been performed for the first band and 73 sets for the second.

After selecting the correct combination differences and using other computer techniques we have found that for the lower common level,  $v'' = 0$ , of the ground state of  $\text{La}^{16}\text{O}$ , the rotational constants are, in the average:

$$B_0'' = 0.35175 \text{ cm}^{-1} \quad \text{and} \quad D_0'' = 0.24 \times 10^{-6} \text{ cm}^{-1}$$

These constants are associated with the two terms expansion of the combination differences, i.e.:

$$\Delta_2 F(J) = 4B_v(J + \frac{1}{2}) - D_v J^2(J + \frac{1}{2})^2. \quad (4)$$

The constants so obtained can be compared with those given in the analysis of Åkerlind<sup>5</sup>.

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