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The Birge Sponer Extrapolation

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I. SYNOPSIS

II. INTRODUCTION

The Birge Sponer (BS) extrapolation is a specialized construct which is used in the Physical Chemistry laboratory to teach about vibrational spectroscopy, visible and ultraviolet spectroscopy, the electronic and vibrational properties of ground state and excited states of diatomic molecules, etc.. It has been incorporated into the standard curriculum because the UV-vis spectrum of I_2(g) is easily obtained and analyzed due to J. Chem. Ed. papers which are endlessly cited [1]. These papers, coupled with Verma's [2] form a basis for many, many discussions of this construct. For more advanced work, some papers which may have been lost on library shelves are worth citing here, i.e., Lessinger [3] which we've used here, and Tellinghuisen [4].

In this piece, a constructed set of data is presented which, *in toto*, allow a student to explore the BS calculation.

III. INVENTED (I_2) DATA

We start with two potential energy curves, one for an excited electronic state, the other for the ground electronic state of a non-existent diatomic molecule. The internuclear distance (R) varies as the nuclei are pulled apart, thereby changing the electronic energy of each state (assuming adiabaticity).

In the upper (excited) state, several vibrational energy levels are shown, while in the lower (ground) state, the lowest vibrational state is shown. The atomic excitation energy is known ($14101\ cm^{-1}$).

The following table shows the energy levels of the vibrational states of the upper electronic state, as well as the separation between energy levels:

It is obvious from the table that this data is fraudulently clean!

Be that as it may, clearly, the difference between frequencies of adjacent vibrational levels in the upper state is tending to zero as the energy levels themselves approach the dissociation limit of the upper electronic energy state, and in fact one can see exactly that the $5\ cm^{-1}$ difference, if maintained will result in about 18 more steps, so that the highest vibrational quantum number with a bound state will be 22+18.

TABLE I: Some Invented (Constructed) Data

$\nu''(cm^{-1})$	$\nu(cm^{-1})$	$\Delta\nu(cm^{-1})$
22	25,419	
		90
23	25,509	
		85
24	25,694	
		80
25	25,774	
		75
26	25,849	
		70
27	25,919	

If we add up all the $\Delta\nu(cm^{-1}$ in the table up to the 22+18 (=40) value, we would get $90+85+80+\cdots$ which would be the total energy "distance" from the lower (22) state to the dissociation limit (40). In the BS, where the data is not so clean, and the separations are themselves decreasing as the quantum number increases, this summation is done graphically using the well known trick that the area under a histogram of stepped heights, whose widths are one (1), is equal to the sum of the step heights.

From the Figures, one sees that the Birge-Sponer area is, approximately,

$$\frac{(40-22)(90)}{2}cm^{-1}$$

which is $810\ cm^{-1}$. Perhaps a better algebraic method for this computation might be that we need

$$5\sum_{i=1} 18i = 5\left(\frac{(18)(19)}{2}\right) = 855$$

Therefore, we have (using the first B.S. extrapolation value)

$$25419 + 810 = 14202 + D.E.$$

which gets us a Dissociation Energy of $12,027\ cm^{-1}$.

IV. REAL DATA

For Iodine, the ground state parameters for the Morse potentials best fit to the actual potential energy function
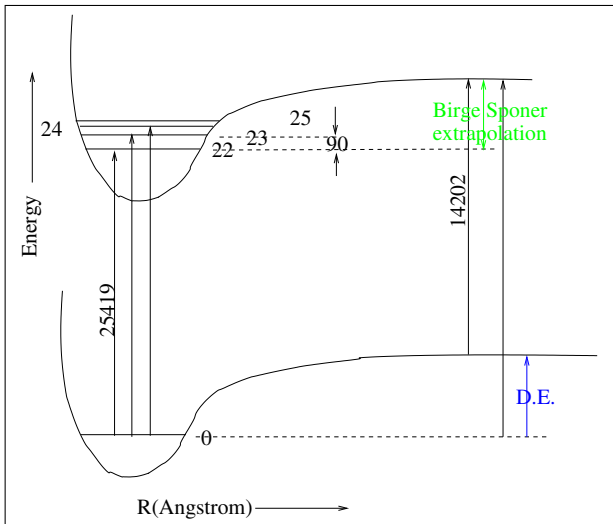
table has been split so as to fit onto one page

FIG. 1: Two diatomic potential energy curves showing the construction of the Birge Sponer extrapolation. Notice that the drawing exaggerates the decrease in separation of energy levels. Also, remember, that in our constructed example this does not occur!
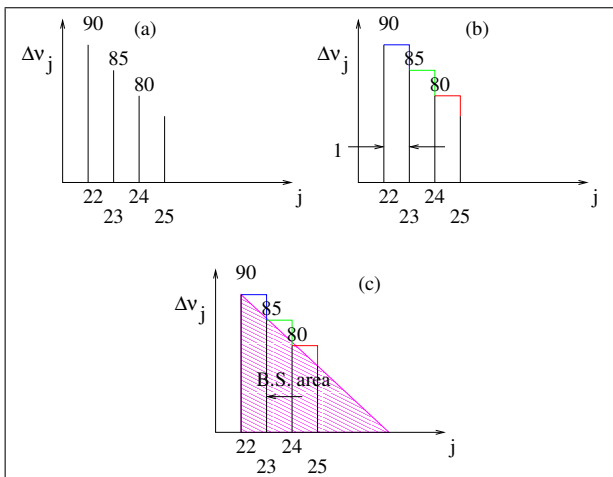

FIG. 2: Part (a) shows the vertical columns whose height we are adding together. Part (b) shows the conversion of these column heights into areas by transforming the heights into parallelograms of width one, so their area numerically equals their heights. Part (c) shows the conversion of Part (b) into a triangular area which is the calculus equivalent of the area sought in Part (b) (which is the sum of heights required in Part (a)), when the standard calculus arguments are made.

gives $\omega_e = 132.1 cm^{-1}$ and $\omega_e x_e = 1.05 cm^{-1}$ with an energy function

$$E_n = \left(n + \frac{1}{2}\right)\omega_e - \omega_2 x_e \left(n + \frac{1}{2}\right)^2$$

with $D_e = 4391 cm^{-1}$, which allows us to write a table such as the following. Parenthetically, we note that the

TABLE II: The first 38 energy levels for the Harmonic Oscillator

Quantum Number	Energy (cm^{-1})	Differences
0	65.79	
1	195.79	130
2	323.69	127.9
3	449.49	125.8
4	573.19	123.7
5	694.79	121.6
6	814.29	119.5
7	931.69	117.4
8	1046.99	115.3
9	1160.19	113.2
10	1271.29	111.1
11	1380.29	109
12	1487.19	106.9
13	1591.99	104.8
14	1694.69	102.7
15	1795.29	100.6
16	1893.79	98.5
17	1990.19	96.4
18	2084.49	94.3
19	2176.69	92.2
20	2266.79	90.1
21	2354.79	88
22	2440.69	85.9
23	2524.49	83.8
24	2606.19	81.7
25	2685.79	79.6
26	2763.29	77.5
27	2838.69	75.4
28	2911.99	73.3
29	2983.19	71.2
30	3052.29	69.1
31	3119.29	67
32	3184.19	64.9
33	3246.99	62.8
34	3307.69	60.7
35	3366.29	58.6
36	3422.79	56.5
37	3477.19	54.4

What we see, at the outset, is that the separation between energy levels is decreasing as we increase the energy (and the quantum number). The separation is approaching zero!

Now the Dissociation Energy for the ground state of I_2 is 4391 cm^{-1}. But you can see from the data in Table III that the crossing point between positive and negative differences in energy occurs at n=62, where the energy is "only" 4154.69 cm^{-1}, a far cry from the reported value (above). Even subtracting the 65.79 cm^{-1} from this value, to obtain the actual energy that a real oscillator would have to find in order to dissociate, does not give us the "reported" value.

As can be seen in Figure 3 the extrapolation to the dissociation limit is clearly visualizeable as a sum of terms for adjacent excitations. Clearly the Birge Sponer extrapolation here is different from the one of the earlier section, in which we dealt with two different electronic states. Here, we're only dealing with one state, the ground electronic state. The idea of the extrapolation, though, is the same.

TABLE III: The highest energy levels for the Harmonic Oscillator

| Quantum Number	Energy (cm^{-1})	Differences
38	3529.49	52.3
39	3579.69	50.2
40	3627.79	48.1
41	3673.79	46
42	3717.69	43.9
43	3759.49	41.8
44	3799.19	39.7
45	3836.79	37.6
46	3872.29	35.5
47	3905.69	33.4
48	3936.99	31.3
49	3966.19	29.2
50	3993.29	27.1
51	4018.29	25
52	4041.19	22.9
53	4061.99	20.8
54	4080.69	18.7
55	4097.29	16.6
56	4111.79	14.5
57	4124.19	12.4
58	4134.49	10.3
59	4142.69	8.2
60	4148.79	6.1
61	4152.79	4
62	4154.69	1.9
63	4154.49	-0.2
64	4152.19	-2.3
65	4147.79	-4.4
66	4141.29	-6.5
67	4132.69	-8.6
68	4121.99	-10.7
69	4109.19	-12.8
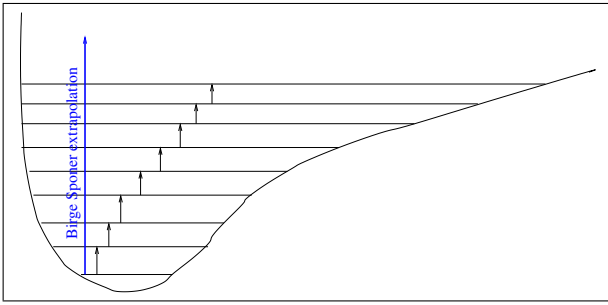
FIG. 3: Birge Sponer extrapolation for a ground electronic state.

V. A BETTER DRAWING OF THE MORSE POTENTIAL AND EIGENFUNCTIONS

When we plot eigenfunctions for the Harmonic Oscillator, we traditionally recenter the wave functions origins by plotting each wave function above a line which represents the eigenenergy (simultaneously representing $\psi = 0$). Such a plot is presented below, as well as the Maple code (from Wang [5]) that did the job.

```
>  #morse potential  from Wang, Physics with
Maple
>  with(plots);
>  V0 := 20; alpha := 1; m := 1; h := 1;
>  lo := -1;n_stop := 10;
>  PE := V0*(1-exp(-alpha*x))^2;
>  xi := 2*sqrt(2*V0*alpha)/(alpha*h)*exp(-alpha*x);
>  En := h*sqrt(2*V0*alpha^2/m)*(n+1/2)-alpha^2*h^2/(2*m)*(n+1/2)^2:
>  s := sqrt(2*(V0-En))/alpha:
>  f := exp(-xi/2)*xi^2*hypergeom([-n],[2*s+1],xi):
>  for i from 0 to n_stop do
>  En||i := eval(En,n=i):
>  f||i := eval(f,n=i):
>  od:
>  for i from 0 to n_stop do
>  F||i := (f||i)/sqrt(evalf(int((f||i)^2,x=-infinity..infinity))):
>  od:
>  plot( [seq(En||n, n =
1..n_stop),seq(F||n+En||n,n=1..n_stop),PE],
>  x=lo..6,0..1.5*V0);
```

$[animate,\ animate3d,\ animatecurve,\ arrow,\ changecoords,\ complexplot,\ complexplot3d,$
$conformal,\ conformal3d,\ contourplot,\ contourplot3d,\ coordplot,\ coordplot3d,$
$cylinderplot,\ densityplot,\ display,\ display3d,\ fieldplot,\ fieldplot3d,\ gradplot,$
$gradplot3d,\ graphplot3d,\ implicitplot,\ implicitplot3d,\ inequal,\ interactive,$
$listcontplot,\ listcontplot3d,\ listdensityplot,\ listplot,\ listplot3d,\ loglogplot,\ logplot,$
$matrixplot,\ odeplot,\ pareto,\ plotcompare,\ pointplot,\ pointplot3d,\ polarplot,$
$polygonplot,\ polygonplot3d,\ polyhedra\_supported,\ polyhedraplot,\ replot,$
$rootlocus,\ semilogplot,\ setoptions,\ setoptions3d,\ spacecurve,\ sparsematrixplot,$
$sphereplot,\ surfdata,\ textplot,\ textplot3d,\ tubeplot]$

$$V0 := 20$$
$$\alpha := 1$$
$$m := 1$$
$$h := 1$$
$$lo := -1$$
$$n\_stop := 10$$
$$PE := 20\,(1 - e^{(-x)})^2$$
$$\xi := 4\,\sqrt{10}\,e^{(-x)}$$
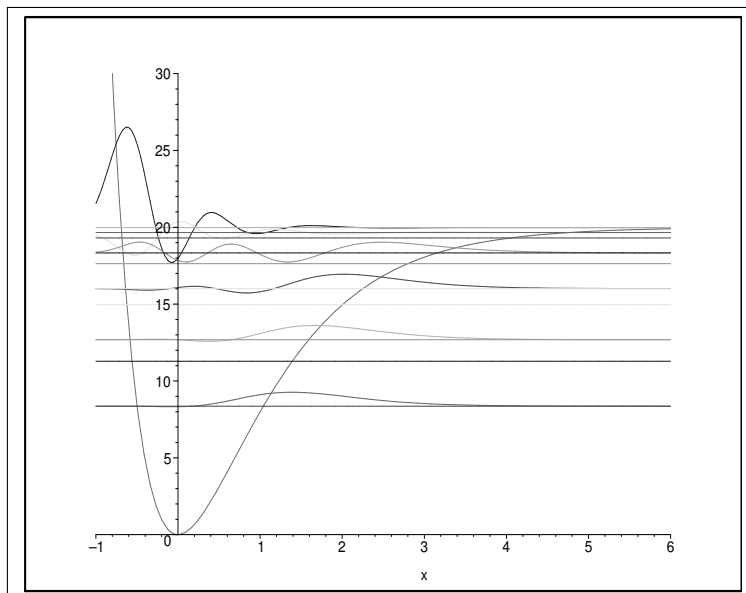
FIG. 4: A Maple rendition of the Morse Potential (due to Wang)

[1] I. J. McNaught, J. Chem. Ed., 64, 919 (1987); F. E. Stafford, J. Chem. Ed., 39, 626 (1962); see also, H. M. Cartwright, J. Chem. Ed., 60, 606 (1983) and S. George, Am. J. Phys. 57, 850 (1989) and R. D'alterio, R. Mattson and R. Harris, J. Chem. Ed., 51m 212 (1974)

[2] R. D. Verma, J. Chem. Phys., 32, 738 (1960); see also E. L. Lewis, G. W. P. Palmer, and J. L. Cruikshank, Am. J. Phys., 62, 350 (1994)., and J. I. Steinfeld, R. N. Zare, L.

Jones, M. Lesl, and W. Klemperer, J. Chem. Phys., 42, 25(1965)

[3] L. Lessinger, J. Chem. Ed., 71, 388 (1994).

[4] J. Telinghuisen, J. Chem. Ed., 58, 438 (1981)

[5] Frank Y. Wang, Physics with Maple, J. Wiley & Sons; the url for downloading worksheets is http://www.wiley-vch.de/publish/en/books/ISBN3-527-40640-9/