ALAMN: Correction to large-r fit of a_λ

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I. BASIC CONCEPTS

Suppose the charge density of a closed-shell N-electron linear molecule be expanded in Legendre polynomials $P_\lambda(\cos\theta)$, viz.,

$$\rho(r,\theta) = \sum_{\lambda=0}^{\lambda_max} a_\lambda(r) P_\lambda(\cos\theta) \tag{1}$$

From the orthogonality relation for the Legendre polynomials, we find that the λth expansion coefficient in Eq. (1) is given as a function of r by

$$a_\lambda(r) = \frac{2\lambda+1}{2} \int_0^\pi \rho(r,\theta) P_\lambda(\cos\theta) \sin\theta \, \mathrm{d}\theta \tag{2}$$

The integral in Eq. (2) is evaluated for values of r in a user-prescribed n-point mesh $\{r_i,\ i = 1, 2, \ldots, n\}$ by a 32-point Gauss-Legendre quadrature.

As r becomes large, the expansion coefficients $a_\lambda(r)$ of the molecular charge density $\rho(r,\theta)$ [Eq. (2)] can be fitted very accurately to the analytic form

$$a_\lambda(r) = A_\lambda r^{p_\lambda} \exp(-\alpha_\lambda r) \tag{3}$$

where A_λ, p_λ and α_λ are real numbers.

In Ref.[1], these parameters are determined by using the last three values of r at which $a_\lambda(r)$ is evaluated from Eq. (2), r_n, r_{n-1} and r_{n-2}. Letting a_n, a_{n-1} and a_{n-2} denote the values of a_λ at these values of r, we have

$$p_\lambda = \frac{h \ln\left(\dfrac{a_{n-1}}{a_n}\right) + \ln\left(\dfrac{a_{n-1}}{a_{n-2}}\right)}{h \ln\left(\dfrac{r_{n-1}}{r_n}\right) + \ln\left(\dfrac{r_{n-1}}{r_{n-2}}\right)} \tag{4}$$

where

$$h = \frac{r_{n-1} - r_{n-2}}{r_n - r_{n-1}} \tag{5}$$

And

$$\alpha_\lambda = \frac{1}{r_{n-1} - r_n} \ln\left[\frac{a_n}{a_{n-1}} \left(\frac{r_{n-1}}{r_n}\right)^{p_\lambda}\right] \tag{6}$$

$$A_\lambda = a_n r_n^{-p_\lambda} \exp(\alpha_\lambda r_n) \tag{7}$$

NOTICE: There is a print error in Eq. (16) in Ref.[1], the source code of ALAMN is consistent with Eq. (7).

Thus the expansion coefficients and hence the charge density need not be calculated for $r > r_n$ even if $a_\lambda(r)$ is required for larger values of r.

II. SAHA'S CORRECTION TO e-N_2

We can get well-behaved large-r a_λ and static potential V_{st} for e-H_2 by using Eq. (3), Eq. (4), Eq. (6) and Eq. (7). But for e-N_2, if we choose the r-mesh as

0.00	0.01	1.20
1.20	0.02	2.00
2.00	0.04	4.40
4.40	0.08	6.00

and choose LAMMAX = 14, we get $A_{14} = 3.093 \times 10^{18}$, $p_{14} = -65.58$ and $\alpha_{14} = -8.408$ for $R = 2.020a_0$. Meanwhile, the static potential (v_λ) for $\lambda = 14$ are

r	v_λ
...	...
5.04000	-0.1131232954588831E+93
5.12000	-0.1410275599185811E+93
5.20000	-0.1752150266189247E+93
5.28000	-0.2169698823790784E+93
5.36000	-0.2678129626035787E+93
5.44000	-0.3295407561285985E+93
5.52000	-0.4042701040798804E+93
5.60000	-0.4944893200460516E+93
5.68000	-0.6031165389052729E+93
5.76000	-0.7335661891117883E+93
5.84000	-0.8898245787188291E+93
5.92000	-0.1076535689486381E+94
6.00000	-0.1299098386733144E+94

They are overflow! (They are too LARGE for other high $\lambda's$ and other internuclear distances!)

I searched our store directory and found that B. C. Saha wrote the following codes in the subroutine ALAM

```
... ... ...
C      PSM=(DLOG(ABY2/ABY1)+RAT*DLOG(ABY2/ABY3))/(DLOG(R2/R1)+RAT*DLOG(R2
```

```
C    #/R3))
c---
      PSM=0.D+00
C     IF(IFIX.EQ.1.AND.PSM.GT.1.D+00) PSM=1.D+00
      QSM = -DLOG((ABY3/ABY2)*(R2/R3)**PSM)/(R3-R2)
C See the note for this modification 8/23/85
      ASM = Y3*R3**(-PSM)*DEXP(QSM*R3)
```

We don't have his note, but from his codes I can guess his formula for large-r a_λ is

$$a_\lambda(r) = A_\lambda \exp(-\alpha_\lambda r) \tag{8}$$

By using Saha's formula we get $A_{14} = 1.351 \times 10^{-3}$, $p_{14} = 0.0$ and $\alpha_{14} = 2.595$. The static potential (v_λ)for $\lambda = 14$ are

r	v_λ
...	...
5.04000	.2155357141168185E-08
5.12000	.1772666466746914E-08
5.20000	.1458346809604667E-08
5.28000	.1200442725400119E-08
5.36000	.9890022814558143E-09
5.44000	.8157512135613536E-09
5.52000	.6738244745961844E-09
5.60000	.5575415032036261E-09
5.68000	.4622160475180030E-09
5.76000	.3839942571407144E-09
5.84000	.3197165625943484E-09
5.92000	.2667999764303344E-09
6.00000	.2231387506188567E-09

III. NEW CORRECTION TO LARGE-R FIT

Although Saha's codes corrected the large-r fit overflow, we can't reproduce e-H_2 static potential because Eq. (8) is different from Eq. (3). I guess that for some e-targets, the

parameters of A_λ, p_λ and α_λ cannot be chosen ONLY by the last three a_λ. So I will fit them by using more $a'_\lambda s$.

Eq. (3) can be rewritten as

$$\ln a_\lambda = \ln A_\lambda + p_\lambda \ln r - \alpha_\lambda r \tag{9}$$

Letting

$$b_\lambda = \ln a_\lambda \tag{10a}$$

$$g_{0\lambda} = \ln A_\lambda \tag{10b}$$

$$g_{1\lambda} = -\alpha_\lambda \tag{10c}$$

$$g_{2\lambda} = p_\lambda \tag{10d}$$

Then

$$b_\lambda = g_{0\lambda} + g_{1\lambda} r + g_{2\lambda} \ln r \tag{11}$$

So b_λ is linearlly dependent on the fitting coefficients. We adopt "General Linear Least Squares" routine — SVDFIT (Signular Value Decomposition fit) [2] to fit the coefficients.

By using 10 a_λ to fit Eq. (11) we get $A_{14} = 2.597 \times 10^{-4}$, $p_{14} = 6.346$ and $\alpha_{14} = 4.627$. The static potential (v_λ) for $\lambda = 14$ are

r	v_λ
...	...
5.04000	0.2154651146898829E-08
5.12000	0.1771786323990111E-08
5.20000	0.1457253305351663E-08
5.28000	0.1199088632125510E-08
5.36000	0.9873308802109118E-09
5.44000	0.8136945736411463E-09
5.52000	0.6713014542439685E-09
5.60000	0.5544554312783496E-09
5.68000	0.4584520410108206E-09
5.76000	0.3794161238428322E-09
5.84000	0.3141632320379888E-09
5.92000	0.2600813953949083E-09
6.00000	0.2150311719575100E-09

By using 80 a_λ to fit Eq. (11) we get $A_{14} = 25.275$, $p_{14} = -10.067$ and $\alpha_{14} = 1.217$. The static potential for $\lambda = 14$ are

r	v_λ
...	...
5.04000	0.2155529635889707E-08
5.12000	0.1772881510956653E-08
5.20000	0.1458613984169379E-08
5.28000	0.1200773569363670E-08
5.36000	0.9894106528899811E-09
5.44000	0.8162537098927050E-09
5.52000	0.6744409210914880E-09
5.60000	0.5582955194052478E-09
5.68000	0.4631357026518250E-09
5.76000	0.3851128268835364E-09
5.84000	0.3210734010977414E-09
5.92000	0.2684415191666285E-09
6.00000	0.2251196654564229E-09

I still keep the linear equation method (LEM) to solve A_λ, p_λ and α_λ by solving Eq. (4), Eq. (6) and Eq. (7). So for H_2, we have two methods to calculate large-r a_λ and static potential (v_λ). For $\lambda = 6$, we get

	LEM	SVDFIT
A_λ	0.1601316757808016E-23	0.1189776202324306E-04
p_λ	0.4523276259430859E+02	0.6724227178999224E+01
α_λ	0.7923329439442724E+01	0.3361975965910192E+01

and static potential (v_λ)

	v_λ (LEM)	v_λ (SVDFIT)
...	...	...
8.90000	-0.3738601412980983E-07	-0.3738604465762323E-07
9.00000	-0.3457238352675295E-07	-0.3457241617130511E-07
9.10000	-0.3199833271303255E-07	-0.3199836759524417E-07
9.20000	-0.2964111789027305E-07	-0.2964115513652894E-07
9.30000	-0.2748037669302244E-07	-0.2748041643535470E-07
9.40000	-0.2549785533465599E-07	-0.2549789771093117E-07
9.50000	-0.2367716973439954E-07	-0.2367721488850992E-07
9.60000	-0.2200359606053337E-07	-0.2200364414259235E-07
9.70000	-0.2046388677921551E-07	-0.2046393794575718E-07
9.80000	-0.1904610885409454E-07	-0.1904616326827752E-07
9.90000	-0.1773950121435192E-07	-0.1773955904616741E-07
10.00000	-0.1653434900198538E-07	-0.1653441042846955E-07

[1] M. A. Morrison, Comp. Phys. Comm. **21**, 63 (1980).

[2] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran 77*, vol. 1 (Press Syndicate of the University of Cambridge, 1997), 2nd ed.