Supplementary Material for "Leading correction to the local density approximation for exchange in large-Z atoms"

Nathan Argaman
Department of Physics, Nuclear Research Center—Negev, P.O. Box 9001, Be'er Sheva 84190, Israel; argaman@mailaps.org

Jeremy Redd
Department of Physics, Utah Valley University, Orem, UT 84058, USA

Antonio C. Cancio
Department of Physics and Astronomy, Ball State University, Muncie, IN 47306, USA

Kieron Burke
Departments of Physics and Astronomy and of Chemistry, University of California, Irvine, CA 92697, USA

(Dated: August 11, 2022)

Tables of exchange-energy data for neutral atoms, positive ions and Bohr atoms are given, as well as details of the fits to asymptotic expansions in the number of electrons.

1. ENERGIES FOR NEUTRAL ATOMS

In Table I we tabulate the per-electron exchange energies $\epsilon_{\rm x} = E_{\rm x}/Z$ (in Ha/electron) for neutral atoms with $1 \leq Z \leq 120$. We include data for the spin-dependent local density approximation (LDA) and the optimized effective potential (OEP).

2. ENERGIES FOR POSITIVE IONS

Table II gives the data for selected positive ions, focusing on a series with the ratio of electron number to nuclear charge, N/Z, set to one-half. The beyond-LDA exchange energy per particle, $\Delta E_{\rm x}/Z = (E_{\rm x} - E_{\rm x}^{\rm LDA})/Z$, is included, and compared with the model suggested in the text: $-B(N/Z)\ln N - C$, with $B(N/Z)$ given by Eq. (18), and $-C$ equal to the beyond LDA value of the Hydrogen atom. The ratio $N/Z = 1/2$ probes a situation roughly halfway between the neutral atom and the Bohr atom, the two limits of Eq. (18) studied in detail. The $\ln Z$ term has been altered to $\ln N$ in order to produce reasonable results in the Bohr-atom limit and for single-electron systems (also included in the table). Replacing $\ln N$ by $\ln Z$ is equivalent to shifting C by $B\ln N/Z$, which is a constant for fixed N/Z. With the use of $\ln N$, the value of C used is 3% off from that for the Bohr atom (see the end of Sec. 4 below).

3. STATISTICAL FITS

In Table III we show systematic data fits for $\Delta E_{\rm x}/Z = (E_{\rm x} - E_{\rm x}^{LDA})/Z$ for the neutral atoms of Table I. The first column indicates the data set used, as explained below, then coefficients with asymptotic standard errors from nonlinear regression, using the Levenberg-Marquardt method. Finally, the reduced χ^2 which is the χ^2 measure divided by the net number of degrees of freedom in the fit. In calculating the reduced χ^2, a standard error of 1 mHa is assumed for individual energy data points.

There are four data sets used here. "all" uses all atoms from $Z = 1$ to 120 indiscriminately. The large data set, "l", consists of 16 data points, corresponding to atoms with closed s, p, d, and f shells, excluding the first occurrence of each series, He ($1s^2$), Ne ($2p^6$), Zn ($3d^{10}$) and Yb ($4f^{14}$). The atoms in the set thus consist of the filled 2s through 8s ($Z = 120$) alkali earths, 3p through 7p ($Z = 118$) noble gases, 4d through 6d group 12 transition metals and the filled 5f actinide. The net number of degrees of freedom varies from 12 to 15, depending on the number of fit parameters. The medium data set, labelled "m", drops the next smallest closed shell of each series, the closed 2s, 3p, 4d and 5f shell atoms, and thus has 12 atoms. The "s" or small data set drops the next smallest shell (3s, 4p, 5d), for 9 atoms.

The basic model used for all fits is [Eq. (2) of main text]:

$$\Delta E_{\rm x}(Z)/Z \approx -(A'Z^{1/3} + B\log Z + C + DZ^{-1/3})$$

which is fit versus $x = Z^{1/3}$, so the actual fit equation used is:

$$y = -A'x - 3B\log x - C - D/x.$$

Assuming $C \neq 0$, there are eight possible models formed by setting A, B or D to be either zero (in which case the data entry is left blank) or nonzero. All eight are shown here for completeness, but in the main text, the fifth, which is noncompetitive is omitted.

Z	LDA	OEP	Z	LDA	OEP	Z	LDA	OEP
1	-0.25643	-0.31250	41	-2.66072	-2.81060	81	-4.18152	-4.34816
2	-0.43087	-0.51288	42	-2.70355	-2.85462	82	-4.21322	-4.38052
3	-0.50477	-0.59358	43	-2.74045	-2.89248	83	-4.24477	-4.41280
4	-0.57258	-0.66644	44	-2.78341	-2.93574	84	-4.27513	-4.44358
5	-0.64936	-0.74854	45	-2.82457	-2.97753	85	-4.30552	-4.47437
6	-0.73837	-0.84105	46	-2.86983	-3.02421	86	-4.33591	-4.50526
7	-0.83672	-0.94349	47	-2.90896	-3.06390	87	-4.36394	-4.53342
8	-0.91253	-1.02256	48	-2.94660	-3.10166	88	-4.39146	-4.56096
9	-0.99989	-1.11145	49	-2.98276	-3.13854	89	-4.41983	-4.58942
10	-1.09667	-1.21050	50	-3.01882	-3.17524	90	-4.44834	-4.61803
11	-1.15723	-1.27391	51	-3.05481	-3.21198	91	-4.48309	-4.65237
12	-1.21362	-1.33236	52	-3.08888	-3.24639	92	-4.51534	-4.68464
13	-1.26815	-1.38945	53	-3.12318	-3.28100	93	-4.54795	-4.71740
14	-1.32461	-1.44808	54	-3.15765	-3.31599	94	-4.58464	-4.75454
15	-1.38288	-1.50894	55	-3.18824	-3.34653	95	-4.61813	-4.78864
16	-1.43435	-1.56220	56	-3.21811	-3.37619	96	-4.64777	-4.81868
17	-1.48856	-1.61782	57	-3.24965	-3.40767	97	-4.68219	-4.85217
18	-1.54512	-1.67637	58	-3.29489	-3.45176	98	-4.71470	-4.88459
19	-1.58748	-1.71931	59	-3.33473	-3.49126	99	-4.74752	-4.91745
20	-1.62795	-1.75995	60	-3.37534	-3.53175	100	-4.78064	-4.95077
21	-1.67794	-1.81033	61	-3.41663	-3.57320	101	-4.81404	-4.98456
22	-1.73095	-1.86381	62	-3.45858	-3.61558	102	-4.84774	-5.01882
23	-1.79706	-1.92995	63	-3.50114	-3.65889	103	-4.87607	-5.04771
24	-1.85542	-1.98981	64	-3.53680	-3.69514	104	-4.90703	-5.07926
25	-1.90284	-2.03933	65	-3.58066	-3.73645	105	-4.93670	-5.10953
26	-1.95511	-2.09125	66	-3.62133	-3.77647	106	-4.96638	-5.13987
27	-2.01567	-2.15052	67	-3.66260	-3.81731	107	-4.99609	-5.17034
28	-2.07288	-2.20820	68	nan	-3.87481	108	-5.02461	-5.19913
29	-2.13180	-2.26810	69	-3.74685	-3.90154	109	-5.05324	-5.22806
30	-2.18308	-2.32063	70	-3.78980	-3.94495	110	-5.08197	-5.25715
31	-2.23125	-2.37083	71	-3.82682	-3.98320	111	-5.11078	-5.28643
32	-2.27892	-2.42026	72	-3.86369	-4.02129	112	-5.13969	-5.31593
33	-2.32634	-2.46958	73	-3.90045	-4.05929	113	-5.16617	-5.34266
34	-2.37021	-2.51475	74	-3.93716	-4.09730	114	-5.19258	-5.36928
35	-2.41456	-2.56025	75	-3.97388	-4.13544	115	-5.21892	-5.39588
36	-2.45932	-2.60647	76	-4.00870	-4.17097	116	-5.24447	-5.42149
37	-2.49740	-2.64514	77	-4.04369	-4.20670	117	-5.27005	-5.44711
38	-2.53421	-2.68227	78	-4.08121	-4.24554	118	-5.29563	-5.47281
39	-2.57363	-2.72217	79	-4.11684	-4.28235	119	-5.31963	-5.49667
40	-2.61419	-2.76329	80	-4.14968	-4.31556	120	-5.34330	-5.52012

TABLE I. Exchange energy per electron for neutral atoms for $Z = 1$ through $Z = 120$, using the PW92 local density approximation (LDA) and the optimized effective potential (OEP).

N	Z	OEP	LDA	$\Delta E_{\rm x}/Z$	model	% difference
1	2	-0.3125	-0.2616	-0.0509	-0.0561	-10.2
2	4	-0.5693	-0.4829	-0.0864	-0.0766	11.4
4	8	-0.7443	-0.6461	-0.0982	-0.0971	1.1
10	20	-1.4872	-1.3591	-0.1280	-0.1241	3.0
12	24	-1.6026	-1.4736	-0.1290	-0.1295	-0.4
18	36	-2.0145	-1.8771	-0.1374	-0.1415	-3.0
1	1	-0.3125	-0.2564	-0.0561	-0.0561	-0.0
1	2	-0.3125	-0.2616	-0.0509	-0.0561	-10.2
1	4	-0.3125	-0.2646	-0.0479	-0.0561	-17.2
1	10	-0.3125	-0.2666	-0.0459	-0.0561	-22.3
1	12	-0.3125	-0.2669	-0.0456	-0.0561	-22.9
1	18	-0.3125	-0.2672	-0.0453	-0.0561	-24.0

TABLE II. Exchange energies divided by Z for various positive ions. Shown are exact exchange using the OEP method, the LDA, the beyond-LDA contribution as compared to an asymptotic model, and the percent error of the model.

data set	A'	B	C	D	χ^2_{red}
all			0.1516(21)		530
l			0.153(6)		560
m			0.158(5)		359
s			0.163(5)		240
all			0.2048(16)	-0.179(5)	41.7
l			0.2138(34)	-0.205(11)	22.1
m			0.2269(25)	-0.256(9)	4.8
s			0.2328(24)	-0.279(9)	2.1
all		0.02432(24)	0.0589(9)		5.8
l		0.02464(26)	0.0590(10)		0.91
m		0.02538(26)	0.0560(11)		0.40
s		0.02535(32)	0.0562(13)		0.29
all		0.0260(9)	0.049(6)	0.013(7)	5.7
l		0.0256(14)	0.053(9)	0.008(12)	0.95
m		0.0238(23)	0.0667(16)	-0.016(23)	0.42
s		0.0225(35)	0.076(24)	-0.03(4)	0.30
all	0.0238(5)		0.0630(17)		21.
l	0.0230(10)		0.067(4)		16.
m	0.021(8)		0.0747(33)		5.8
s	0.0199(8)		0.0807(34)		3.0
all	0.0149(5)		0.1189(30)	-0.0759(39)	5.1
l	0.0128(9)		0.134(5)	-0.098(7)	1.3
m	0.0103(10)		0.154(7)	-0.136(12)	0.43
s	0.0090(14)		0.165(11)	-0.155(20)	0.33
all	0.0032(11)	0.0212(12)	0.0590(9)		5.5
l	0.0007(15)	0.0239(16)	0.0592(11)		0.96
m	-0.0013(20)	0.0285(35)	0.0549(20)		0.42
s	-0.0025(28)	0.0269(24)	0.0533(36)		0.30
all	0.014(4)	0.008(7)	0.117(19)	-0.073(24)	5.1
l	-0.007(8)	0.039(16)	0.01(5)	0.06(7)	0.98
m	0.003(17)	0.02(4)	0.09(15)	-0.05(20)	0.47
s	-0.025(35)	0.08(8)	-0.16(34)	0.3(5)	0.33

TABLE III. Coefficients and statistics for data fits to neutral atoms. Coefficients match those of Eq. (2) and Table I of the main text.

4. THE BOHR ATOM

The exchange energies for the Bohr atom were fit by defining a residual

$$R_o(N) = [E_{\rm x}^{\rm Bohr}(N) + \bar{A}_o N^{5/3}]/N \,,$$

in lieu of $E_{\rm x}^{\rm Bohr}(N)$ itself (recall that $\bar{A}_o = (2/3)^{1/3}(4/\pi^2)$). The values of this residual are provided in Table IV for up to $n = 22$ full shells, and are seen to vary nearly linearly in $\ln N$, with the deviations from linearity decreasing for large N. In order to obtain many-digit accuracy for the coefficients, a second residual,

$$S_o(N) = [R_o(N) + \bar{B}_o \ln N + \bar{C}_o]N^{2/3} \,,$$

was defined, and it too varies nearly linearly in $\ln N$. The most accurate fit was obtained by inspecting visually plots of $S_o(N) + \bar{D}_o \ln N$ vs. $\ln N$, magnifying the deviation of the second residual from linearity in $\ln N$, and adjusting the values of the coefficients so that the deviations from linearity at large N are minimal [once it was guessed that $\bar{B}_o = 7/(27\pi^2)$, the analytic value was used for subsequent refinement, so that no more than two coefficients needed to be simultaneously adjusted]. Obtaining smooth plots requires retaining more than 6 significant digits in $R_o(N)$, due to the multiplication by $N^{2/3}$ and the magnification (even more significant digits are required in $E_{\rm x}^{\rm Bohr}(N)$, of course).

For the LDA applied to the Bohr atom, a residual $R_o^{\rm LDA}(N)$ was similarly defined, with values given in Table V. In this case the deviations from linearity are greater, due to the presence of additional terms in the expansion — here, the second residual would be defined with a power of $N^{1/3}$ rather than $N^{2/3}$. The similarity of the $\propto N$ and the $\propto N^{2/3}\ln N$ behaviors over a large range of N makes fitting by visual inspection difficult (the accuracy achieved for $\bar{B}_o^{\rm LDA}$ based on data up to $n = 28$ shells was circa 1%, leaving some room for questions regarding the use of the analytic value). Luckily, extension of the data set to very large values of N is accessible, up to $n = 100$ shells here, and an automated fit provides sufficient accuracy (which is gauged by comparison to fits with more limited ranges of data).

The fit gives $\bar{B}_o^{\rm LDA} = -7.505$ mHa and $\bar{C}_o^{\rm LDA} = -9.2$ mHa (further coefficients were not carefully extracted). Extracting the beyond-LDA coefficient as in Eq. (12) gives $C_o = 54.6$ mHa for the Bohr atom, which differs by only a few percent from the neutral-atom value in Eq. (3).

n	N	$R_o(N)$
1	2	-0.06298252
2	10	-0.10453258
3	28	-0.13185039
4	60	-0.15211566
5	110	-0.16821274
6	182	-0.18156344
7	280	-0.19296926
8	408	-0.20292569
9	570	-0.21176023
10	770	-0.21970057
11	1012	-0.22691143
12	1300	-0.23351580
13	1638	-0.23960797
14	2030	-0.24526180
15	2480	-0.25053622
16	2992	-0.25547902
17	3570	-0.26012950
18	4218	-0.26452035
19	4940	-0.26867906
20	5740	-0.27262896
21	6622	-0.27639005
22	7590	-0.27997958

TABLE IV. The residual of the exchange energy per electron for Bohr atoms with n complete shells. N is the number of electrons.

n	N	$R_o^{\mathrm{LDA}}(N)$	n	N	$R_o^{\mathrm{LDA}}(N)$	n	N	$R_o^{\mathrm{LDA}}(N)$	n	N	$R_o^{\mathrm{LDA}}(N)$
1	2	0.02594248	26	12402	0.08262241	51	91052	0.09663426	76	298452	0.10511544
2	10	0.03499465	27	13860	0.08339534	52	96460	0.09704426	77	310310	0.10539532
3	28	0.04156255	28	15428	0.08414161	53	102078	0.09744674	78	322478	0.10567170
4	60	0.04657061	29	17110	0.08486301	54	107910	0.09784198	79	334960	0.10594467
5	110	0.05059082	30	18910	0.08556118	55	113960	0.09823025	80	347760	0.10621431
6	182	0.05394465	31	20832	0.08623759	56	120232	0.09861179	81	360882	0.10648071
7	280	0.05682234	32	22880	0.08689356	57	126730	0.09898682	82	374330	0.10674393
8	408	0.05934382	33	25058	0.08753032	58	133458	0.09935556	83	388108	0.10700407
9	570	0.06158899	34	27370	0.08814897	59	140420	0.09971824	84	402220	0.10726118
10	770	0.06361357	35	29820	0.08875052	60	147620	0.10007504	85	416670	0.10751533
11	1012	0.06545792	36	32412	0.08933592	61	155062	0.10042615	86	431462	0.10776661
12	1300	0.06715218	37	35150	0.08990601	62	162750	0.10077175	87	446600	0.10801506
13	1638	0.06871947	38	38038	0.09046158	63	170688	0.10111202	88	462088	0.10826076
14	2030	0.07017791	39	41080	0.09100336	64	178880	0.10144712	89	477930	0.10850376
15	2480	0.07154194	40	44280	0.09153204	65	187330	0.10177720	90	494130	0.10874413
16	2992	0.07282331	41	47642	0.09204822	66	196042	0.10210242	91	510692	0.10898191
17	3570	0.07403166	42	51170	0.09255251	67	205020	0.10242291	92	527620	0.10921717
18	4218	0.07517502	43	54868	0.09304543	68	214268	0.10273881	93	544918	0.10944996
19	4940	0.07626018	44	58740	0.09352751	69	223790	0.10305025	94	562590	0.10968033
20	5740	0.07729287	45	62790	0.09399920	70	233590	0.10335737	95	580640	0.10990833
21	6622	0.07827803	46	67022	0.09446095	71	243672	0.10366027	96	599072	0.11013401
22	7590	0.07921992	47	71440	0.09491317	72	254040	0.10395907	97	617890	0.11035741
23	8648	0.08012225	48	76048	0.09535626	73	264698	0.10425388	98	637098	0.11057859
24	9800	0.08098825	49	80850	0.09579058	74	275650	0.10454481	99	656700	0.11079758
25	11050	0.08182080	50	85850	0.09621647	75	286900	0.10483197	100	676700	0.11101443

TABLE V. The residual for the Bohr atom within the LDA.