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Commentationes

Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

I. Nuclear Magnetic Shielding Constants*

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Nuclear magnetic shielding constants σ have been evaluated for all the positive ions, neutral atoms, and negative ions up to Krypton ($Z = 36$). Extrapolated values (up to $Z = 106$) are also presented for these systems. Comparison with previously calculated σ is made wherever such values are available. It is pointed out that the contribution to σ of an electron is independent of its orbital angular momentum quantum number but depends upon the principal quantum number of the shell, and that innermost shells make the largest contribution.

Die kernmagnetischen Abschirmungskonstanten σ sind für alle positiven Ionen, neutrale Atome und negativen Ionen bis zum Krypton ($Z = 36$) berechnet und bis $Z = 106$ extrapoliert worden. Den Ergebnissen werden soweit möglich – anderweitig berechnete σ-Werte gegenübergestellt. Es wird gezeigt, daß der Beitrag eines Elektrons zu σ unabhängig von seinen Nebenquantenzahl ist, daß er aber von der Hauptquantenzahl der Schale abhängt und daß die innersten Schalen den größten Beitrag liefern.

Les constantes d'écran magnétique nucléaire σ ont été calculées pour tous les ions positives, les atomes neutres et les ions négatives jusqu'au Krypton ($Z = 36$). On présente aussi des valeurs extrapolées (jusqu'à $Z = 106$) pour tous ces systèmes et on établit une comparaison avec les valeurs calculées par des autres auteurs. On remarque que la contribution d'un électron à la valeur de σ est indépendante de son nombre quantique orbital, mais pas de son nombre quantique principal, et on montre que les couches électroniques intérieures donnent la contribution la plus important.

Introduction

The theoretical determination of physical properties, which constitutes by itself one of the goals of quantum-mechanical calculations, is now becoming a reality as more and more accurate wave functions are made available, mostly the so-called Hartree-Fock functions, for both atoms and molecules.

Two distinct groups of physical properties must be considered; i.e., those associated with one-electron operators and the properties which correspond to two-electron operators. Taking into account that Hartree-Fock functions do not include practically any electronic correlation they should be used, in principle, only for the evaluation of one-electron properties.

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The purpose of this series of papers is to present the results of a research project undertaken at this laboratory for the determination of physical properties, such as nuclear magnetic shielding, diamagnetic susceptibility, electric field gradient, nuclear quadrupole coupling constant, etc., for all atoms and their positive and negative ions for which Hartree-Fock functions are available, as well as for the isoelectronic series.

Theoretical Considerations

Larmor's theorem states that the presence of an external magnetic field H does not change (to first order in H) the electronic motion in a many-electron system, except for the appearance of the so-called Larmor precession. Its effect is to create a shielding field at the nucleus which, though small as compared to the external field, constitutes an important correction in connection with the measurement of nuclear magnetic moments by the Kusch-Rabi resonance method [*11*].

An expression for this shielding field was derived by Lamb [*12*], who showed it to depend directly on the electrostatic potential produced by the electrons at the nucleus. Evaluating the electrostatic potential on the basis of the statistical Thomas-Fermi-Dirac (TFD) model of an atom Lamb derived, for the ratio of the induced to the external field, the expression

$$10^5\, H'(0)/H = \sigma\, 10^5 = -3.19\, Z^{\frac{4}{3}}\,, \tag{1}$$

where Z is the nuclear charge of the nucleus.

The calculation of σ, the nuclear magnetic shielding constant, is in principle very simple, once the corresponding wave function is known, taking into account that σ is related to the expectation value of the inverse of the distance of the electrons from the nucleus.

So σ for a ^1S state of an N-electron atom or ion is given, as shown by Hylleraas [*10*] and Dickinson [*4*], by

$$\sigma = \tfrac{1}{3}\,\alpha^2 \langle \Phi \,|\, \sum_{i=1}^{N} r_i^{-1} \,|\, \Phi \rangle \tag{2}$$

where α is the fine structure constant and r_i is the distance of the i^{th} electron from the nucleus (in a.u.), with the summation extending over all the electrons in the system; Φ is the wave function for the system under consideration.

The first calculation was performed by Hylleraas [*10*] using his accurate wave function for He. Almost simultaneously Dickinson [*4*] reported nuclear magnetic shielding constants for a large number of atoms and ions, evaluated from Hartree (H) or Hartree-Fock (HF) functions.

A large number of workers have recently reported the values of shielding constants, determined from various functions. Rustgi and Tiwari [*16*], using the best HF functions of Roothaan, Sachs and Weiss [*14*], calculated σ for systems with two, three, and four electrons. Ellison [*6, 7*] used the rescaled functions of Ellison and Huff [*5*] also for atomic systems with up to four electrons. Strand and Bonham [*19*] obtained approximate analytical expressions for the electronic potential for HF functions of atoms up to $Z = 36$ by fitting the radial electron density with analytical expressions by least squares, and Bonham and Strand [*2*] evaluated the nuclear magnetic shielding constants using these expressions. More recently Saxena and Narasinhan [*17*] have reported the shielding constants for rare gases, calculated from the Hartree-Fock-Slater (HFS) functions of Herman and Skillman [*9*].

However, a systematic study of the shielding constants has not been attempted so far using HF functions. With the development of efficient computer programs in recent years, accurate analytical HF functions have been made available for all the atoms up to $Z = 36$, and also for their positive and negative ions. In this paper the nuclear magnetic shielding constants evaluated from HF functions are reported.

Calculations

The wave functions used in the present calculations are the HF functions determined by Clementi [*3*], except that for the second row neutral atoms ($Z = 11$ to 18) the functions of Malli [*13*] and for Cr ($Z = 24$), Mo and Mo^+ ($Z = 42$), Xe ($Z = 54$), and Rn ($Z = 86$) those of Synek [*15, 20, 21*] were used.

In order to be able to extrapolate the present results to higher Z values, the calculated values have been fitted by a three-parameter formula,

$$\sigma = k\,(Z' - s)^t\,, \tag{3}$$

the optimum values of the parameters having been determined in the following manner. Using an initial value t_0, with $s = 0$, one determines the average value of k which best fits the calculated values as a whole. With this values of k, and again $s = 0$, one now determines the average value of t, and finally, using the average values of k and t, one finds the average value of s. It is realized that there can be better fitting procedures, but the present method has been found to be quite adequate for the calculations reported (see below). It must be pointed out that in Eq. (3) Z' stands for a corrected nuclear charge, equal to the number of electrons in the system; i.e., $Z' = Z$ for neutral systems, and $Z' = Z \pm 1$ for negative and positive ions, respectively.

Results and Discussion

The nuclear magnetic shielding constants σ calculated for neutral atoms, using the functions mentioned in the prededing section (with the exception of Rn), are presented in Tab. 1, where existing calculated values are also included for comparison.

It is easily seen in this Table that the σ_{TFD}, calculated with the TFD functions of Bonham and Strand [*1*] are always greater than the σ_{H}, calculated using H functions reported by Dickinson [*4*], the σ_R presented by Ellison [*6, 7*], and the σ_{HF} reported in this paper. It can be seen that σ_{TFD} is as much as 50% greater for $Z = 2$; this discrepancy is reduced to 40% for $Z = 3$, decreases steadily with increasing Z until it is 20% for $Z = 10$, 10% for $Z = 22$, 7.7% for $Z = 30$, and 4% for $Z = 36$, while the remaining σ's agree among themselves within 0.2 — 0.5% up to $Z = 10$. It would seem that the TFD functions are not suitable for the calculation of the expectation values of one-electron operators, at least for atoms up to $Z = 36$. This is expected as the TFD is a statistical model and will be applicable more accurately to a heavy atom than to a light atom. As σ is a one-electron property, which depends upon the electronic density, one can conclude that the AHF, HF, HFS, H, and R functions are equally accurate in describing the electronic densities for light atoms. This is reasonable as the exchange effects do not play a very important role in light atoms; the exchange density can be

Table 1. *Nuclear magnetic shielding constants*[a] ($\sigma \cdot 10^5$) *for groundstates of neutral atoms*

Z	σ_{HF}	σ_{AHF}	σ_{HFS}	σ_{FHF}	σ_{H}	σ_{R}	σ_{TFD}
2	5.990	6.002	6.0	5.99	6.00	5.985	8.937
3	10.145	10.145		10.145	10.1	10.421	14.313
4	14.926	14.926		14.932	14.9	15.303	20.562
5	20.199			20.207	19.9	20.203	27.21
6	26.074			26.102	26.1	26.068	34.16
7	32.547			32.561	32.5	32.524	41.38
8	39.511			39.526	39.5	39.443	48.88
9	47.071			47.083	46.4	47.003	56.65
10	55.226		56.3	55.108	54.7	55.108	64.69
11	62.887			63.087	62.9		72.97
12	70.859			71.222	71.0		81.50
13	78.986			79.392	79.5		90.27
14	87.406			87.870	88.1		99.26
15	96.111			96.664	97.0		108.5
16	105.044			105.67	106.0		117.9
17	114.262			114.96	115.0		127.5
18	123.760		125.4	124.53	124.0		137.2
19	132.934			134.55	133.0		147.2
20	142.285			144.30	142.0		157.3
21	152.134			142.49[b]	151.0		167.6
22	162.274			163.50	161.0		178.0
23	172.664			174.00	171.0		188.5
24	183.650			184.78	181.0		199.2
25	194.201			195.83	191.0		210.1
26	205.287			207.06	202.0		221.0
27	216.635			218.57	214.0		232.1
28	228.231			230.29	226.0		243.3
29	240.473			242.24	238.0		254.6
30	252.166			254.48	249.0		266.1
31	263.856			266.45	261.0		277.6
32	275.707			278.43	273.0		289.2
33	287.716			290.87	285.0		301.0
34	299.838			303.32	296.0		312.8
35	312.119			315.95	308.0		324.7
36	324.559		327.4	328.74	321.0		336.7
42	400.323				397.0		
54	563.847		567.8		559.0		
86	1072.0		1076.8		1060.0		

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[a] The notation used in this Table is as follows:

σ_{HF}: values, reported in this paper, calculated using the functions of CLEMENTI [*3*], MALLI [*13*], ROOTHAAN and SYNEK [*15*], and SYNEK [*20, 21*].

σ_{AHF}: values, reported by RUSTGI and TIWARI [*16*], calculated from the accurate analytical Hartree-Fock functions of ROOTHAAN, SACHS and WEISS [*14*].

σ_{HFS}: values, reported by SAXENA and NARASIMHAN [*16*], calculated using the Hartree-Fock-Slater functions given by HERMAN and SKILLMAN [*9*].

σ_{FHF}: values, reported by BONHAM and STRAND [*2*], calculated using approximate analytical expressions for the Hartree-Fock potential, obtained by fitting the radial electron density with an analytical expression by least squares (STRAND and BONHAM [*19*]).

σ_{H}: values, reported by DICKINSON [*4*], calculated using Hartree, Hartree-Fock, or extrapolated Hartree functions from several sources, given by DICKINSON [*4*].

σ_{R}: values, reported by ELLISON [*6, 7*], calculating using the rescaled functions obtained by ELLISON and HUFF [*5*].

σ_{TFD}: values, reported by BONHAM and SRTAND [*2*] calculated using the approximate analytical Thomas-Fermi-Dirac functions reported by BONHAM and STRAND [*1*].

[b] The discrepancy in this value is probably due to a typographical error.

adequately approximated by Slater's [*18*] "free-electron gas" density and reasonably good analytical fits to the HF functions can be obtained using the scaling procedure or by the use of a few parameters, at least for light atoms.

However, for heavier atoms one finds that σ_{HF}, σ_{HFS}, σ_{FHF}, and σ_{H} differ as much as 1%, for $Z = 30$, with σ_{FHF} and σ_{H} differing by 2%, for $Z = 36$, while σ_{HF} and σ_{HFS} differ only by 1%. Furthermore, σ_{HF} and σ_{H} agree to within 1% up to $Z = 54$, and therefore one must conclude that the exchange effects do not play an important role in determining one-electron properties.

Investigating the values of σ_{HF} and σ_{H} in particular, one finds the following behaviour: $\sigma_{\mathrm{HF}} > \sigma_{\mathrm{H}}$ from $Z = 2$ to 10, agreeing to 1%; $\sigma_{\mathrm{HF}} < \sigma_{\mathrm{H}}$ from $Z = 11$ to 19, differing by 0.7% at the most; and finally $\sigma_{\mathrm{HF}} > \sigma_{\mathrm{H}}$ again for $Z = 20$ to 36, with their values agreeing to 1%. Furthermore, it has been observed that $\sigma_{\mathrm{HF}} = \frac{1}{2}(\sigma_{\mathrm{FHF}} + \sigma_{\mathrm{H}})$, for $Z = 2$ to 11 and $Z = 22$ to 36, where $\sigma_{\mathrm{FHF}} > \sigma_{\mathrm{HF}} > \sigma_{\mathrm{H}}$ (but not from $Z = 11$ to 19, where $\sigma_{\mathrm{FHF}} > \sigma_{\mathrm{H}} > \sigma_{\mathrm{HF}}$).

Table 2. *Partial contributions (in percentages) to σ from the various electronic shells in Xenon*

Shell	Electronic population[a] (%)	Contribution (%) to σ
1*s*	3.7	33.3
2*s*	3.7	7.8
3*s*	3.7	2.8
4*s*	3.7	1.2
5*s*	3.7	0.4
2*p*	11.0	23.2
3*p*	11.0	8.4
4*p*	11.0	3.3
5*p*	11.0	1.0
3*d*	18.5	13.6
4*d*	18.5	4.7

[a] Percentage of the number of electrons in the shell, referred to the total number of electrons in the atom.

Tab. 2 collects the individual contributions to σ of the various electronic shells of Xe. Two important conclusions can be obtained from this Table. One can observe first that although the 1*s* electrons constitute only a 3.7% of the total number of electrons of the system, they contribute 33.3% to the total σ. This is expected because σ is related to the average reciprocal distance of *all* the electrons in the atoms and the nearest electrons to the nucleus are those in the 1*s* shell, and hence they should contribute most. This is an unfortunate situation because for heavy atoms (and in our example one is already considering Xe, with $Z = 54$) the relativistic effects are very pronounced, and this is especially true for the innermost shells, where the electrons are moving at very high speeds, comparable to the speed of light.

A second fact, far more important, can also be observed in Tab. 2. One can see, for example, that the contribution to σ of the 6 electrons in the 2*p* shell is precisely three times that of the 2 electrons in the 2*s* shell, i.e., the contribution per electron seems to be independent of the orbital angular momentum quantum number, depending only on the principal quantum number. Similar conclusions can be reached by inspection of the contributions from the 3*s* and 3*p* shells, 4*s* and 4*p* shells, etc. In addition, supporting this fact, one also has that the contributions of the 3*d* and 3*p* shells are in the ratio 5:3, while the shells 3*d* and 3*s* contribute in the ratio 5:1. All this is in agreement with the fact that the average of the distance of an electron from the nucleus depends almost exclusively upon the principal quantum number of the shell into which the electron is accommodated.

Table 3. *Nuclear magnetic shielding constants*[a] ($\sigma \cdot 10^5$) *for groundstates of positive and negative ions of atoms*

Z	positive	negative	Z	positive	negative
3	9.540	10.419	20	141.844	
4	14.149		21	151.957	152.630
5	19.381	20.651	22	162.102	162.812
6	25.107	26.696	23	172.500	173.242
7	31.430	33.205	24	183.158	183.953
8	38.350	40.317	25	193.993	194.798
9	45.766	48.021	26	205.099	205.933
10	53.775		27	216.451	217.311
11	62.382	63.150	28	228.045	230.761
12	70.271		29	239.906	240.821
13	78.444	79.328	30	251.550	
14	86.774	87.861	31	263.320	264.198
15	95.392	96.600	32	275.090	276.156
16	104.292	105.623	33	287.056	288.185
17	113.426	114.930	34	299.162	300.372
18	122.843		35	311.387	312.719
19	132.540	133.148	36	323.776	

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[a] Evaluated using the analytical Hartree-Fock functions determined by CLEMENTI [*3*].

In Tab. 3 the σ for the positive and negative ions of atoms up to $Z = 36$ are presented.

Tab. 4, 5 and 6 presents the values for the magnetic shielding constants for a few excited states of neutral atoms, and their positive and negative ions. Almost all these excited states correspond to the same configurations as for ground states of the systems presented in Tab. 1 and 3. The only exceptions are the states ^1S and ^3S of He, which correspond to the configuration $(1s)$ $(2s)$, and for which the function of FRAGA and BIRSS [*8*] has been used. As it can be seen the difference with the values of the corresponding groundstates is practically negligible.

Table 4. *Nuclear magnetic shielding constants*[a] ($\sigma \cdot 10^5$) *for some excited states of neutral atoms*

Atom	State		Atom	State	
He[b]	^1S	4.196	*P*	^2P	96.055
	^3S	4.074	*S*	^1D	105.022
C	^1D	26.031		^1S	104.989
	^1S	25.965	Cr	^5D	183.302
N	^2D	32.484	Cu	^2D	240.069
	^2P	32.441	Ge	^1D	275.688
O	^1D	39.468	As	^2D	287.687
	^1S	39.405		^2P	287.669
Si	^1D	87.383	Se	^1D	299.817
	^1S	87.344		^1S	299.793
P	^2D	96.078			

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[a] Evaluated using the analytical Hartree-Fock functions determined by CLEMENTI [*3*] and MALLI [*13*].

[b] These excited states correspond to the electronic configuration $(1s)$ $(2s)$, as evaluated by FRAGA and BIRSS [*8*].

Table 5. *Nuclear magnetic shielding constants*[a] ($\sigma \cdot 10^5$) *for some excited states of positive ions*

Atom	State		Atom	State	
N	^1D	31.391	S	^2P	104.244
	^1S	31.328	Cl	^1D	113.411
O	^3P	38.249		^1S	113.379
	^2D	38.290	As	^1D	287.042
F	^1D	45.726		^1S	287.016
	^1S	45.667	Se	^2D	299.137
P	^1D	95.371		^2P	299.121
	^1S	95.330	Br	^1D	311.374
S	^2D	104.262		^1S	311.350

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[a] Evaluated using the analytical Hartree-Fock functions determined by CLEMENTI [*3*].

Table 6. *Nuclear magnetic shielding constants*[a] ($\sigma \cdot 10^5$) *for some excited states of negative ions*

Atom	State		Atom	State	
B	^1D	20.578	Si	^2P	87.779
	^1S	20.622	P	^1D	96.570
C	^2D	26.617		^1S	96.528
	^2P	26.562	Ga	^1D	264.149
N	^1D	33.155	Ge	^2D	276.108
	^1S	33.080		^2P	276.077
Al	^1D	79.277	As	^1D	288.156
	^1S	79.193		^1S	288.120
Si	^2D	87.815			

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[a] Evaluated using the analytical Hartree-Fock functions determined by CLEMENTI [*3*].

Table 7. *Fitted values for the nuclear magnetic shielding constants* ($\sigma \cdot 10^5$) *for groundstates of neutral atoms*

Z	neutral atoms	positive ions	negative ions	Z	neutral atoms	positive ions	negative ions
2	5.896			23	172.937	175.690	172.627
3	10.332	7.625	12.930	24	183.425	186.210	183.290
4	15.382	12.961	17.734	25	194.081	196.873	194.158
5	20.945	18.884	23.005	26	204.902	207.674	205.228
6	26.953	25.287	28.702	27	215.883	218.608	216.494
7	33.359	32.099	34.792	28	227.022	229.673	227.955
8	40.127	39.272	41.251	29	238.314	240.866	239.605
9	47.228	46.768	48.057	30	249.756	252.182	251.442
10	54.639	54.560	55.191	31	261.346	263.619	263.463
11	62.339	62.624	62.638	32	273.080	275.174	275.665
12	70.313	70.941	70.384	33	284.955	286.845	288.044
13	78.545	79.495	78.418	34	296.969	298.629	300.599
14	87.025	88.271	86.728	35	309.119	310.524	313.326
15	95.740	97.258	95.305	36	321.404	322.526	326.223
16	104.680	106.446	104.140	37	333.819	334.636	339.287
17	113.838	115.824	113.226	38	346.364	346.848	352.518
18	123.204	125.385	122.554	39	359.036	359.164	365.911
19	132.772	135.122	132.120	40	371.834	371.580	379.465
20	142.536	145.026	141.915	41	384.754	384.095	393.178
21	152.488	155.092	151.935	42	397.796	396.706	407.048
22	162.624	165.315	162.174	43	410.957	409.412	421.074

Table 7 (Fortsetzung)

Z	neutral atoms	positive ions	negative ions	Z	neutral atoms	positive ions	negative ions
44	424.237	422.212	435.252	77	920.049	889.489	979.860
45	437.632	435.104	449.582	78	936.619	904.833	998.466
46	451.142	448.087	464.063	79	953.271	920.238	1017.185
47	464.766	461.159	478.691	80	970.003	935.704	1036.017
48	478.501	474.320	493.465	81	986.816	951.230	1054.960
49	492.346	487.566	508.385	82	1003.709	966.817	1074.015
50	506.299	500.898	523.448	83	1020.681	982.463	1093.180
51	520.360	514.314	538.653	84	1037.732	998.167	1112.454
52	534.528	527.814	553.999	85	1054.860	1013.931	1131.838
53	548.800	541.395	569.483	86	1072.066	1029.752	1151.330
54	563.175	555.057	585.106	87	1089.349	1045.631	1170.929
55	577.653	568.798	600.865	88	1106.708	1061.567	1190.636
56	592.233	582.618	616.760	89	1124.143	1077.559	1210.449
57	606.912	596.516	632.788	90	1141.653	1093.607	1230.368
58	621.690	610.491	648.950	91	1159.238	1109.712	1250.392
59	636.567	624.541	665.243	92	1176.897	1125.871	1270.520
60	651.540	638.667	681.667	93	1194.630	1142.085	1290.753
61	666.610	652.866	698.220	94	1212.436	1158.354	1311.089
62	681.774	667.139	714.901	95	1230.315	1174.677	1331.528
63	697.033	681.484	731.710	96	1248.266	1191.053	1352.070
64	712.384	695.900	748.645	97	1266.289	1207.483	1372.713
65	727.828	710.387	765.706	98	1284.384	1223.966	1393.457
66	743.363	724.944	782.890	99	1302.549	1240.501	1414.302
67	758.989	739.570	800.198	100	1320.785	1257.088	1435.247
68	774.705	754.265	817.628	101	1339.091	1273.726	1456.292
69	790.509	769.028	835.180	102	1357.466	1290.417	1477.436
70	806.401	783.857	852.852	103	1375.911	1307.158	1498.679
71	822.381	798.754	870.644	104	1394.424	1323.950	1520.020
72	838.447	813.715	888.554	105	1413.006	1340.792	1541.459
73	854.598	828.742	906.583	106	1431.655	1357.684	1562.994
74	870.835	843.834	924.728	107	1450.373	1374.626	1584.627
75	887.156	858.989	942.990	108		1391.618	1606.356
76	903.561	874.208	961.368				

Tab. 7 presents the values fitted for the three types of systems, in their ground-states. The optimum fitting parameters found are the following: $k = 2.2603$, $s = 0$, $t = 1.3833$, for neutral systems; $k = 3.079$, $s = 0$, $t = 1.3083$, for positive ions; and $k = 1.5430$, $s = -0.2035$, $t = 1.4804$, for negative ions.

The accuracy of the fitting can be best checked by inspection of the values for neutral systems, and making use of the general rule drawn from Tab. 2. Because the program used for the calculations could handle only orbitals with an azimuthal quantum number of up to 2, it was not possible to complete the calculation for Rn, even if the wave function is available. But applying the ratios found in the discussion of Tab. 2, it was possible to estimate the contribution of the 14 electrons in the $4f$ shell, yielding a total value of $1072.0 \cdot 10^{-5}$ for σ, which compares extraordinarily well with the fitted value of $1072.01 \cdot 10^{-5}$.

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Note added: Computer print-outs of the expectation values of the one-electron operators r^{-1}, r^{-2}, z^2, z^2/r^{-3}, and z^2/r^{-5} for all the neutral atoms ($Z = 2$ to 36, 42, 54), positive ions ($Z = 3$ to 36, 42), and negative ions ($Z = 3$ to 35) are available (in limited amount) upon request.

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