

Regular article

Average inner product sums of electron linear momenta for atoms and ions

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Abstract. From the second moments of the electron-pair densities in momentum space, accurate Hartree–Fock values of the average inner product sum $\langle \sum_{i<j} \mathbf{p}_i \cdot \mathbf{p}_j \rangle$ of electron linear momenta are evaluated for the 102 neutral atoms from He to Lr, the 53 singly charged cations from Li^+ to Cs^+ , and the 43 stable anions from H^- to I^- in their experimental ground states. The present results are new for 38 species and improve the literature values for 68 species.

Key words: Inner products of linear momenta – Electron-pair densities – Neutral atoms – Singly charged ions

1 Introduction

Usually the nonrelativistic total energies of atoms and ions are discussed with the neglect of the contribution from the motion of nucleus. To take the nuclear motion contribution into account, we add the mass polarization (specific mass) correction [1],

$$\varepsilon_{\text{mp}} = S/M, \quad (1)$$

to the total energy, where M is the nuclear mass and S is the average inner product sum of the electron momenta defined by

$$S \equiv \left\langle \sum_{i<j=1}^N \mathbf{p}_i \cdot \mathbf{p}_j \right\rangle, \quad (2)$$

in which N is the number of electrons and \mathbf{p}_i is the linear momentum operator of the i th electron. The mass polarization correction, ε_{mp} , plays an important role for the atomic isotope shift [2] and is closely related to the first moment of the oscillator strength density [3] and the momentum correlation coefficient [4].

Though the values of ε_{mp} or S were calculated from various types of wave functions in the literature [5, 6, 7,

8, 9, 10, 11, 12], systematic and consistent data for atoms and ions are available only at the Hartree–Fock level: Lo and Fraga (LF) [5] reported the S values for neutral atoms and singly charged ions from He (atomic number $Z=2$) to Kr ($Z=36$), using approximate Roothaan–Hartree–Fock wave functions. However, an excited state instead of the ground state was considered for the Cr atom, four cations ($Z=21, 22, 25, 26$) and two anions ($Z=21, 28$). Bauche [6] calculated numerical Hartree–Fock S values for 15 atoms from the alkali, alkali-earth, and transition atoms. The most extensive compilation of the Hartree–Fock mass polarization correction was given by Fraga and coworkers (FKS) [7] for atoms and cations from $Z=5$ to 102, but the ground states were not examined for many atoms and ions.

When the neutral atoms with $Z \leq 103$ and singly charged ions with $N \leq 54$ are examined, however, we find that the ground-state data are missing in the literature [5, 6, 7] for 16 neutral atoms, six cations, and 16 anions. Moreover, our comparison of the literature S values [5, 6, 7] showed some discrepancy in many atoms. For example, Bauche [6] reports $S=5,911$ for the Os atom, but FKS [7] say $S=5,907$. The insufficient accuracy was also pointed out [13] for the FKS Hartree–Fock calculations. Therefore, we decided to determine accurate Hartree–Fock values of the sums S by using a rigorous equality,

$$S = \langle P^2 \rangle - \frac{1}{4} \langle v^2 \rangle, \quad (3)$$

which was found [14] very recently. In Eq. (3), $\langle P^2 \rangle$ and $\langle v^2 \rangle$ are the second moments of the electron-pair extracule (center-of-mass motion) and intracule (relative motion) densities in momentum space, respectively, and their Hartree–Fock limit values are established in the literature [15, 16] for the 102 neutral atoms from He to Lr, the 53 singly charged cations from Li^+ to Cs^+ , and the 43 stable anions from H^- to I^- in their experimental ground states. We are well aware of the fact [8, 9, 10, 11, 12] that there is a non-negligible difference between Hartree–Fock and correlated values. It is worth, however, summing up accurate Hartree–Fock S values, since it is not easy to perform correlated calculations for

heavier species and, by definition, the Hartree–Fock values are the starting point in the analysis of correlation contributions. The next section outlines our computational procedure. The S values are presented for the 102 neutral atoms and the 96 ions in Sect. 3, and they are compared with the literature values. The present results are new for 16 neutral atoms and 22 ions, and improve the literature values for 45 neutral atoms and 23 ions. Hartree atomic units are used throughout.

2 Computational outline

The experimental ground electronic configurations and terms [17, 18, 19] were considered for all the 102 neutral atoms from He to Lr, the 53 cations from Li^+ to Cs^+ , and the 43 anions from H^- to I^- . There are two exceptions, however. For the anions Sc^- and Pd^- , the experimental ground states were reported [19] to be $4s^2 3d 4p, ^1D$ and $5s 4d^{10} ^2S$, but the Hartree–Fock method does not give [20] meaningful solutions to these states. Thus, the second lowest states, $4s^2 3d^2 ^3F$ for Sc^- and $5s^2 4d^9 ^2D$ for Pd^- , were examined instead.

The electron-pair moments $\langle v^2 \rangle$ and $\langle P^2 \rangle$ in momentum space to be used in Eq. (3) were taken from Ref. [15] for the 102 neutral atoms and from Ref. [16] for the 96 ions. As is clear from Eq. (3), the sum S originates from the cancellation of the positive extracule and negative intracule contributions; therefore, we used more significant figures for the electron-pair moments than those tabulated in Refs. [15, 16]. The accuracy and consistency of these moment data were checked for each species by a sum rule [21],

$$\langle v^2 \rangle + 4\langle P^2 \rangle - 2(N-1)\langle p^2 \rangle = 0, \quad (4)$$

where $\langle p^2 \rangle$ is the single-electron second moment in momentum space.

3 Results and discussion

LF [5] and Bauche [6] gave the S values in atomic units, while FKS [7] gave the ϵ_{mp} values in reciprocal centimeters. We converted the FKS data to S values in atomic units using $S = \epsilon_{\text{mp}}(m + M)/(2mR_M)$, where $m = 548.579 \times 10^{-6}$ amu [22] is the electron mass and R_M is the Rydberg constant for finite nuclear mass. The values of M and R_M were taken from Table AI(1) of the Ref. [7] for consistency.

For the neutral atoms, the present S values are shown in Fig. 1a as a function of Z . The values increase monotonically with increasing Z . In the Hartree–Fock approximation, the first three atoms, He, Li, and Be, with only s orbitals have $S = 0$, i.e., $\langle P^2 \rangle$ is equal to $\langle v^2 \rangle/4$ [15].

When the present results are compared with the LF values [5] for 31 neutral atoms ($Z = 5\text{--}36$, except 24), the LF data for 24 atoms agree with ours to 4–6 figures, but the values for the other seven atoms ($Z = 8, 9, 16, 18, 28, 33, 36$) are reliable only to three significant figures. We find no difference between the present values and those of Bauche [6] for two atoms with $Z = 19$ and 94 among the 15 atoms, but the agreement is four or five significant figures for the other 13 atoms. FKS reported [7] the ground-state ϵ_{mp} values for 82 atoms. For the 29 light atoms ($Z = 5\text{--}34$, except 24), their ϵ_{mp} have only three figures or less, but the derived S values agree with ours in the given number of figures. For the heavier 53 atoms ($Z = 35\text{--}102$, except 41, 42, 44, 45, 57, 58, 64, 78, 89–93, 96, 97), however, comparison of the present and FKS data shows that the

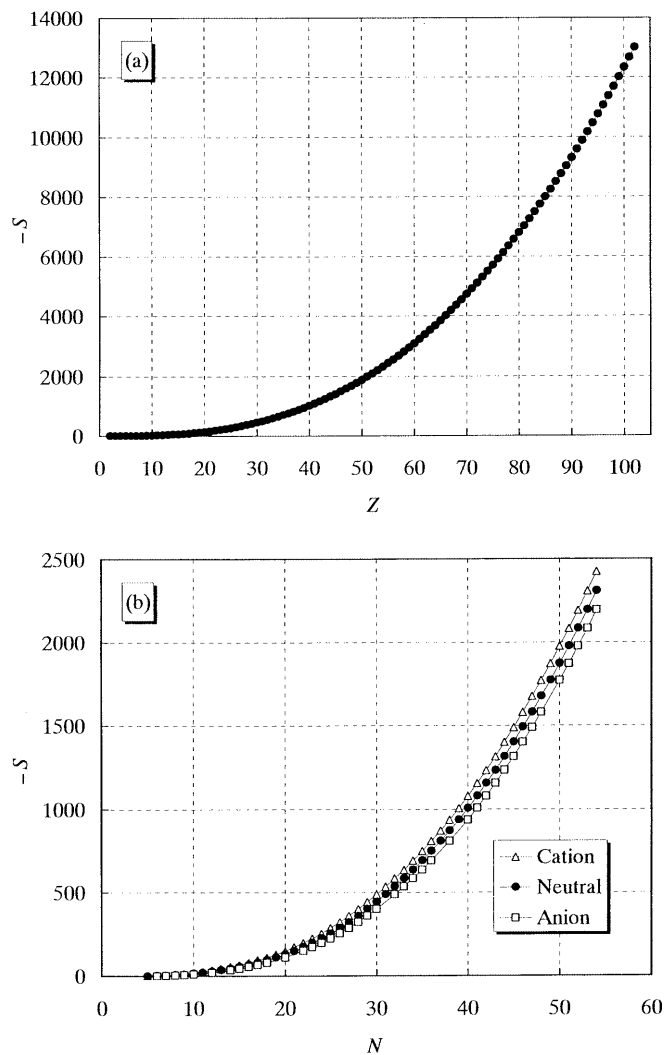


Fig. 1a, b. Average inner product sums of electron linear momenta. **a** The neutral atom values as a function of Z . **b** The ion values as a function of N

accuracy of the latter values is limited to three significant figures in 50 atoms, which exclude $Z = 40, 43$, and 47 from the 53 atoms. By combining all these examinations of the present and the literature [5, 6, 7] values, we find that among the 102 neutral atoms, the present results are new for 16 atoms and improve the literature values for 45 atoms, where we have considered the literature values are insufficiently accurate if they have three or less reliable figures. The inner product sums of electron linear momenta for 99 atoms are summarized in Table 1 along with the valence configurations and the terms of their experimental ground states.

By comparing the results for the cations in this study with the LF values [5] for 27 species ($Z = 6\text{--}36$, except 21, 22, 25, 26), we find that the agreement between the two sets of data is four or five significant figures for 23 cations, but the LF values for the other four cations ($Z = 9, 31, 32, 34$) have three significant figures. Among the 19 singly charged cations with $Z = 35\text{--}55$ (except 40 and 43), the FKS values [7] agree with ours to four significant figures for four cations ($Z = 41, 46, 47, 50$), but to three significant

Table 1. The average inner product sums of electron linear momenta for 99 neutral atoms. For $Z=2-4$, $S=0$ in the Hartree–Fock theory

Z	Configuration	Term	$-S$	Z	Configuration	Term	$-S$
5	$2p$	2P	0.404858	55	$6s$	2S	2,426.84
6	$2p^2$	3P	1.39418	56 ^b	$6s^2$	1S	2,547.26
7	$2p^3$	4S	3.17939	57 ^a	$5d$	2D	2,671.40
8 ^b	$2p^4$	3P	5.84970	58 ^a	$4f5d$	1G	2,802.54
9 ^b	$2p^5$	2P	9.71244	59 ^b	$4f^3$	4I	2,941.09
10	$2p^6$	1S	14.9780	60	$4f^4$	5I	3,080.91
11	$3s$	2S	20.8031	61 ^b	$4f^5$	6H	3,225.02
12	$3s^2$	1S	27.6107	62	$4f^6$	7F	3,373.57
13	$3p$	2P	35.5926	63 ^b	$4f^7$	8S	3,526.63
14	$3p^2$	3P	44.8314	64 ^a	$4f^75d$	9D	3,680.71
15	$3p^3$	4S	55.4244	65 ^b	$4f^9$	6H	3,845.60
16 ^b	$3p^4$	3P	67.4164	66	$4f^{10}$	5I	4,012.07
17	$3p^5$	2P	80.9456	67 ^b	$4f^{11}$	4I	4,183.19
18 ^b	$3p^6$	1S	96.1088	68 ^b	$4f^{12}$	3H	4,359.02
19	$4s$	2S	112.446	69 ^b	$4f^{13}$	2F	4,539.69
20	$4s^2$	1S	130.242	70	$4f^{14}$	1S	4,725.31
21	$3d$	2D	150.652	71 ^b	$5d$	2D	4,912.14
22	$3d^2$	3F	173.282	72 ^b	$5d^2$	3F	5,103.23
23	$3d^3$	4F	198.161	73 ^b	$5d^3$	4F	5,298.62
24 ^a	$4s3d^5$	7S	226.385	74 ^b	$5d^4$	5D	5,498.41
25	$3d^5$	6S	255.125	75 ^b	$5d^5$	6S	5,702.68
26	$3d^6$	5D	287.218	76	$5d^6$	5D	5,911.35
27	$3d^7$	4F	322.020	77 ^b	$5d^7$	4F	6,124.61
28 ^b	$3d^8$	3F	359.590	78 ^a	$6s5d^p$	3D	6,343.49
29	$4s$	2S	401.461	79 ^b	$6s$	2S	6,566.15
30	$4s^2$	1S	443.510	80 ^b	$6s^2$	1S	6,792.28
31	$4p$	2P	488.073	81 ^b	$6p$	2P	7,022.94
32	$4p^2$	3P	535.131	82	$6p^2$	3P	7,258.09
33 ^b	$4p^3$	4S	584.769	83 ^b	$6p^3$	4S	7,497.77
34	$4p^4$	3P	637.009	84 ^b	$6p^4$	3P	7,741.96
35	$4p^5$	2P	691.952	85 ^b	$6p^5$	2P	7,990.74
36 ^b	$4p^6$	1S	749.656	86 ^b	$6p^6$	1S	8,244.14
37	$5s$	2S	809.711	87 ^b	$7s$	2S	8,501.79
38 ^b	$5s^2$	1S	872.389	88 ^b	$7s^2$	1S	8,763.94
39 ^b	$4d$	2D	938.338	89 ^a	$6d$	2D	9,030.88
40	$4d^2$	3F	1,007.37	90 ^a	$6d^2$	3F	9,302.47
41 ^a	$5s4d^4$	6D	1,080.12	91 ^a	$5f^26d$	4K	9,583.65
42	$5s4d^5$	7S	1,155.49	92 ^a	$5f^36d$	5L	9,867.92
43	$4d^5$	6S	1,233.24	93 ^a	$5f^46d$	6L	10,157.4
44 ^a	$5s4d^7$	5F	1,315.74	94	$5f^6$	7F	10,454.5
45 ^a	$5s4d^8$	4F	1,400.84	95 ^b	$5f^7$	8S	10,754.7
46 ^b	$4d^{10}$	1S	1,490.14	96 ^a	$5f^76d$	9D	11,057.5
47	$5s$	2S	1,581.31	97 ^a	$5f^86d$	8H	11,368.1
48 ^b	$5s^2$	1S	1,675.49	98 ^b	$5f^{10}$	5I	11,686.7
49	$5p$	2P	1,772.94	99 ^b	$5f^{11}$	4I	12,008.3
50 ^b	$5p^2$	3P	1,873.64	100 ^b	$5f^{12}$	3H	12,335.4
51 ^b	$5p^3$	4S	1,977.65	101 ^b	$5f^{13}$	2F	12,668.0
52 ^b	$5p^4$	3P	2,084.94	102 ^b	$5f^{14}$	1S	13,006.3
53 ^b	$5p^5$	2P	2,195.62	103 ^a	$6d$	2D	13,346.9
54 ^b	$5p^6$	1S	2,309.71				

^a New results

^b Improvements of literature values

figures for the other 15 cations. On the basis of this comparison, we find six new and 17 improved S values for cations, which are shown in Table 2. For the 25 anions ($Z=5-35$, except 10, 12, 18, 20, 28, 30), a comparison of the LF values [5] with our data for the anions shows that six anions ($Z=5, 8, 14, 24, 25, 31$) have three significant figures and the other 19 anions have 4–6 significant figures. Accordingly, we obtain 16 new and six improved values for the anions as given in Table 2.

The Hartree–Fock S values of cations, atoms, and anions with $N \leq 54$ are compared in Fig. 1b as a function of N . The three cations (Li^+ , Be^+ , B^+) and two anions

(H^- and Li^-) satisfy $S=0$ for the same reason as their isoelectronic neutral atoms. We introduce a symbol $S(N, Z)$ for the S value of a species with N electrons and atomic number Z . Figure 1b shows that for an isoelectronic series with the same N (5 or greater), the inequality

$$S(N, Z+1) < S(N, Z) < S(N, Z-1) \quad (5)$$

holds with no exception. On the other hand, a comparison of neutral atoms and ions with the same Z shows that the approximate equality

$$S(N-1, Z) \cong S(N, Z) \cong S(N+1, Z) \quad (6)$$

Table 2. The average inner product sums of electron linear momenta for 50 singly charged cations and 41 anions. For cations with $Z=3-5$ and anions with $Z=1$ and 3 , $S=0$ in the Hartree–Fock theory

Cation				Anion			
Z	Configuration	Term	$-S$	Z	Configuration	Term	$-S$
6	$2p$	2P	0.880856	5 ^b	$2p^2$	3P	0.535698
7	$2p^2$	3P	2.54971	6	$2p^3$	4S	1.60530
8	$2p^3$	4S	5.21690	7	$2p^4$	3P	3.36898
8 ^b	$2p^4$	3P	8.94353	8 ^b	$2p^5$	2P	6.12720
9 ^b	$2p^5$	2P	14.0643	9	$2p^6$	1S	10.0887
10	$2p^6$	1S	20.7892	11	$3s^2$	1S	20.8042
11	$3s$	2S	27.5871	13	$3p^2$	3P	35.6676
12	$3s^2$	1S	35.3883	14 ^b	$3p^3$	4S	44.9568
13	$3p$	2P	44.5632	15	$3p^4$	3P	55.5538
14	$3p^2$	3P	55.0871	16	$3p^5$	2P	67.5985
15	$3p^3$	4S	67.0578	17	$3p^6$	1S	81.1866
16	$3p^4$	3P	80.5096	19	$4s^2$	1S	112.448
17	$3p^5$	2P	95.5897	21	$3d^2$	3F	151.305
18	$3p^6$	1S	112.394	22	$3d^3$	4F	174.064
19	$4s$	2S	130.177	23	$3d^4$	5D	199.051
21 ^a	$4s3d$	3D	150.608	24 ^b	$3d^5$	6S	226.430
22 ^a	$4s3d^2$	4F	173.245	25 ^b	$3d^6$	5D	256.050
23	$3d^4$	5D	199.156	26	$3d^7$	4F	288.279
24	$3d^5$	6S	226.537	27	$3d^8$	3F	323.172
25 ^a	$4s3d^5$	7S	255.098	28 ^a	$3d^9$	2D	360.833
26 ^a	$4s3d^6$	6D	287.219	29	$3d^{10}$	1S	401.421
27	$3d^8$	3F	323.353	30	$4s$	2S	443.615
28	$3d^9$	2D	361.034	31 ^b	$4s^2$	1S	487.867
29	$3d^{10}$	1S	401.636	32 ^b	$4p$	2P	534.868
30	$4s$	2S	443.615	33	$4p^2$	3P	584.447
31 ^b	$4s^2$	1S	487.867	34	$4p^3$	4S	637.191
32 ^b	$4p$	2P	534.868	35	$4p^4$	3P	584.906
33	$4p^2$	3P	584.447	36	$4p^5$	2P	637.191
34 ^b	$4p^3$	4S	636.674	37 ^a	$4p^6$	1S	692.183
35	$4p^4$	3P	691.554	39 ^a	$5s^2$	1S	809.714
36	$4p^5$	2P	749.194	40 ^a	$4d5p$	1D	938.331
37 ^b	$4p^6$	1S	809.648	41 ^a	$4d^3$	4F	1,007.91
38 ^b	$5s$	2S	872.310	42 ^a	$4d^4$	5D	1,080.13
39 ^b	$5s^2$	1S	937.606	43 ^a	$4d^5$	6S	1,155.52
40 ^a	$5s4d^2$	4F	1,007.32	44 ^a	$4d^6$	5D	1,233.98
41	$4d^4$	5D	1,080.19	45 ^a	$4d^7$	4F	1,315.74
42 ^b	$4d^5$	6S	1,155.58	46 ^a	$4d^8$	3F	1,400.83
43 ^a	$5s4d^5$	7S	1,233.19	47 ^a	$4d^9$	2D	1,489.31
44 ^b	$4d^7$	4F	1,315.83	48 ^a	$4d^{10}$	1S	1,581.28
45 ^b	$4d^8$	3F	1,400.92	49 ^a	$5p^2$	3P	1,773.03
46	$4d^9$	2D	1,489.41	50 ^a	$5p^3$	4S	1,873.77
47	$4d^{10}$	1S	1,581.39	51 ^a	$5p^4$	3P	1,977.77
48 ^b	$5s$	2S	1,675.53	52 ^a	$5p^5$	2P	2,085.11
49 ^b	$5s^2$	1S	1,772.73	53 ^a	$5p^6$	1S	2,195.82
50	$5p$	2P	1,873.38				
51 ^b	$5p^2$	3P	1,977.33				
52 ^b	$5p^3$	4S	2,084.63				
53 ^b	$5p^4$	3P	2,195.25				
54 ^b	$5p^5$	2P	2,309.28				
55 ^b	$5p^6$	1S	2,426.77				

^a New results

^b Improvements of literature values

is valid for larger Z . Equation (6) implies that the S values depend predominantly on core electrons, as demonstrated [6] by a decomposition of the S values into core–core, core–valence, and valence–valence contributions for six atoms with $Z=12, 19, 42, 60, 70$, and 76 .

4 Summary

By using the intracule $\langle v^2 \rangle$ and extracule $\langle P^2 \rangle$ moments of the electron-pair densities in momentum space, we

have obtained accurate Hartree–Fock expectation values of the inner product sums of linear momenta for 102 atoms from He to Lr, for 53 cations from Li^+ to Cs^+ , and for 43 anions from H^- to I^- . The present results are new for 38 species and improve the literature values for 68 species.

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