

## Letter

# Correlated electron-pair properties of the Li atom in momentum space

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**Abstract.** On the basis of multiconfiguration Hartree–Fock calculations, correlated electron-pair intracule (relative motion) and extracule (center-of-mass motion) properties are reported for the Li atom in momentum space. The present results are more accurate and consistent than those in the literature.

**Key words:** Electron-pair densities – Moments – Correlation effects – Li atom – Momentum space

### 1 Introduction and definitions

For an explicit examination of the electron–electron interaction in many-electron atoms, the electron-pair intracule (relative motion),  $H(u)$ , and extracule (center-of-mass motion),  $D(R)$ , densities,

$$H(u) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(u - |\mathbf{r}_i - \mathbf{r}_j|) \right\rangle, \quad (1)$$

$$D(R) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(R - |\mathbf{r}_i + \mathbf{r}_j|/2) \right\rangle,$$

have been introduced [1] and studied [2, 3, 4, 5], where  $\delta(x)$  is the one-dimensional Dirac delta function and the angled brackets stand for the expectation value over the  $N$ -electron ( $N \geq 2$ ) wave function  $\psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  with  $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$  being the combined position-spin coordinates of electron  $i$ . The  $H(u)$  and  $D(R)$  densities are the probability density functions for the interelectronic distance  $|\mathbf{r}_i - \mathbf{r}_j|$  and the center-of-mass radius  $|\mathbf{r}_i + \mathbf{r}_j|/2$  of any pair of electrons  $i$  and  $j$  for  $u$  and  $R$ , respectively, and are normalized to  $N(N-1)/2$ , the number of electron pairs. The moments associated with the electron-pair densities  $H(u)$  and  $D(R)$  are defined by

$$\langle u^n \rangle \equiv \int_0^\infty du u^n H(u), \quad \langle R^n \rangle \equiv \int_0^\infty dR R^n D(R) \quad (2)$$

and characterize the distributions of the parent densities. In particular,  $\langle u^{-1} \rangle$  is nothing but the electron repulsion energy,  $\langle u \rangle$  is the average interelectronic distance, and  $\langle R \rangle$  is the average distance of electron pairs from the nucleus. The corresponding intracule  $\bar{H}(v)$  and extracule  $\bar{D}(P)$  densities in momentum space, as well as their moments  $\langle v^n \rangle$  and  $\langle P^n \rangle$ , have also been studied [5]:

$$\bar{H}(v) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(v - |\mathbf{p}_i - \mathbf{p}_j|) \right\rangle, \quad (3)$$

$$\bar{D}(P) \equiv \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(P - |\mathbf{p}_i + \mathbf{p}_j|/2) \right\rangle,$$

$$\langle v^n \rangle \equiv \int_0^\infty dv v^n \bar{H}(v), \quad \langle P^n \rangle \equiv \int_0^\infty dP P^n \bar{D}(P), \quad (4)$$

where  $p_i$  is the momentum vector of electron  $i$ . The densities  $\bar{H}(v)$  and  $\bar{D}(P)$  and the moments  $\langle v^n \rangle$  and  $\langle P^n \rangle$  have physical meanings analogous to those of their position-space counterparts, but in momentum space.

In a recent article [6], it was shown that precise and consistent knowledge of the electron-pair moments is important, because in addition to their own significance, the four types of the second electron-pair moments  $\langle u^2 \rangle$ ,  $\langle R^2 \rangle$ ,  $\langle v^2 \rangle$  and  $\langle P^2 \rangle$  are directly related to several physical properties, which have been hitherto studied independently. Moreover, these second moments were demonstrated [7] to satisfy rigorous sum rules,

$$\delta_{\text{pos}} \equiv 4\langle R^2 \rangle + \langle u^2 \rangle - 2(N-1)\langle r^2 \rangle = 0, \quad (5)$$

$$\delta_{\text{mom}} \equiv 4\langle P^2 \rangle + \langle v^2 \rangle - 2(N-1)\langle p^2 \rangle = 0, \quad (6)$$

for any exact and approximate wave functions of atoms and molecules, where  $\langle r^2 \rangle$  and  $\langle p^2 \rangle$  are the second single-electron moments in position and momentum spaces, respectively.

At the Hartree–Fock limit level, the electron-pair properties in both position and momentum spaces were established [8, 9, 10, 11, 12, 13, 14] for all the 102 neutral atoms from He to Lr in their ground states. At the correlated level, however, the electron-pair properties were not known in a consistent manner except for the He atom [15]. In the case of the Li atom, the next atom in the periodic table, relatively accurate data were reported for the intracule [16, 17, 18] and extracule [18] properties in position space. In momentum space, on the other hand, Sarsa et al. [19, 20] have published correlated electron-pair data of the Li atom based on Monte Carlo calculations. However, a closer examination shows that the results of Sarsa et al. are inconsistent and insufficiently accurate in that the second moments do not satisfy the sum rule, the total energy of the parent wave function is rather poor, and the virial error is nontrivial. Therefore, we decided to perform correlated calculations of the momentum-space electron-pair properties of the Li atom in a more accurate, yet consistent, manner, and the results are reported here. Hartree atomic units are used throughout.

## 2 Computational outline

We first constructed a multiconfiguration Hartree–Fock (MCHF) wave function using a modified version of the MCHF88 program [21]. By referring to the 18 and 21 configuration wave functions given by Froese Fischer [22], we obtained a 30-configuration MCHF function, which consists of  $1s^22s$ ,  $2sns^2$  ( $n = 3-6$ ),  $2snp^2$  ( $n = 2-5$ ),  $2snd^2$  ( $n = 3-6$ ),  $2snf^2$  ( $n = 4-6$ ),  $2sng^2$  ( $n = 5-7$ ),  $2snh^2$  ( $n = 6, 7$ ),  $2s7i^2$ ,  $1sns^2$  ( $n = 2, 3$ ),  $2s^23s$ ,  $1s2p3p$ ,  $1snp6p$  ( $n = 2-4$ ), and  $1s6p^2$  electron configurations. Our MCHF total

energy,  $E$ , is  $-7.477229$  hartrees, which recovers 98.2% of the correlation energy in the Li atom [17]. The deviation in the virial ratio,  $-E/T$ , from unity is  $2 \times 10^{-9}$ , where  $T$  is the electronic kinetic energy. All the electron-pair densities and moments were then evaluated by the procedure described in Ref. [23]. Talman’s algorithm [24] was employed for the required numerical Hankel transformation from position- to momentum-space functions.

## 3 Results and discussion

To check the reliability of the MCHF calculations, we first computed the electron-pair properties in position space. The results are summarized and compared with the literature values [9, 10, 16, 17, 18, 20, 25] in Table 1, where the columns are arranged in decreasing order of the total energies of the parent wave functions. When the intracule moments  $\langle u^n \rangle$  are compared, the present values show satisfactory agreements with those of Gálvez et al. [18] and Yan and Drake [16] with lower total energies. The changes in  $\langle u^n \rangle$  from their Hartree–Fock values [9] are in accord with the fact [18] that the electron correlation effect increases the radial density  $H(u)$  in an intermediate- $u$  region ( $0.66 < u < 4.35$ ) and decreases  $H(u)$  in small- $u$  ( $0 < u < 0.66$ ) and large- $u$  ( $u > 4.35$ ) regions. In this respect, the correlated Monte Carlo  $\langle u^n \rangle$  values reported by Sarsa et al. [25] appear erratic, since their  $\langle u^n \rangle$  values with  $n > 0$  are incorrectly predicted to be larger than the corresponding Hartree–Fock values. The three sets of correlated extracule moments  $\langle R^n \rangle$  in Table 1 are similar and their changes from the Hartree–Fock values [10] correctly reflect the correlation contribution [18] in the extracule density  $D(R)$  that the density is shifted from a large- $R$  to a small- $R$  region on

**Table 1.** Electron-pair properties of the Li atom in position space

	Hartree–Fock [9, 10]	Correlated				
		Gálvez et al. [20]	Sarsa et al. [25]	Present	Gálvez et al. [18]	Yan and Drake [16, 17]
<b>Energies</b>						
$E$	-7.43273	-7.4738	-7.47669	-7.47723	-7.478058	-7.478060
$-E/T$	1.00000	0.99957	–	1.00000	–	1.000000
<b>Intracule moments</b>						
$\langle u^{-2} \rangle$	5.03229	–	4.372	4.40404	4.39	–
$\langle u^{-1} \rangle$	2.28092	–	2.1778	2.19820	2.1998	2.19821
$\langle u \rangle$	8.68909	–	9.007	8.68566	8.669	8.66840
$\langle u^2 \rangle$	37.2641	–	40.31	37.0092	36.85	36.8478
$\langle u^3 \rangle$	195.834	–	222.8	193.355	192.2	–
$\langle u^4 \rangle$	1187.09	–	–	1165.74	1156	–
<b>Extracule moments</b>						
$\langle R^{-2} \rangle$	20.1292	20.56	–	20.1760	20.21	–
$\langle R^{-1} \rangle$	4.56184	4.6141	–	4.59506	4.6013	–
$\langle R \rangle$	4.34454	4.3062	–	4.30910	4.2996	–
$\langle R^2 \rangle$	9.31603	9.137	–	9.18585	9.145	–
$\langle R^3 \rangle$	24.4793	23.71	–	24.0178	23.86	–
$\langle R^4 \rangle$	74.1929	70.90	–	72.4573	71.83	–
<b>Other two–electron properties</b>						
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$	0	–	–	-0.0665	-0.0675	-0.0694
$S(-1)$	12.4214	–	–	12.2035	12.1483	12.1440
$\tau[\mathbf{r}]$	0	–	–	-0.0036	-0.0037	–
<b>Sum-rule check</b>						
$\langle r^2 \rangle_{\text{pos}}$	18.6321	–	–	18.4382	18.359	18.3546
$\delta_{\text{pos}}$	0.0000	–	–	0.0000	-0.006	–

the whole. (In more detail,  $D(R)$  increases at  $0.12 < R < 0.58$  and  $0.93 < R < 1.63$ , while it decreases at  $0 < R < 0.12$ ,  $0.58 < R < 0.98$ , and  $R > 1.65$ .) The table also lists the inner product,  $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$ , the minus first moment,  $S(-1)$ , of the dipole oscillator strength density [26, 27], and the statistical angular correlation coefficient,  $\tau[\mathbf{r}]$  [28]. Their values are not very different among the three correlated studies. The last entry in Table 1 gives a sum-rule check,  $\delta_{\text{pos}}$ , defined by Eq. (5). The vanishing  $\delta_{\text{pos}}$  value in the present calculations shows that the intracule and extracule properties are consistently obtained. However, we find an inconsistency ( $\delta_{\text{pos}} = -0.006$ ) for the data of Gálvez et al. [18].

The momentum-space electron-pair properties obtained from the present MCHF calculations are summarized and compared with the literature values [9, 10, 16, 17, 19, 20, 29] in Table 2. The columns of the table are again arranged in decreasing order of the associated total energies. When compared with the Hartree–Fock values [9],  $\langle v^n \rangle$  are found to increase if  $n < 0$  and to decrease if  $n > 0$  upon the inclusion of the electron correlation. However, the previous calculations by Sarsa et al. [19] predicted that the correlated  $\langle v^{-2} \rangle$  and  $\langle v^{-1} \rangle$  values are incorrectly smaller than the corresponding Hartree–Fock results. The correlation contribution,  $\Delta\bar{H}(v)$ , in momentum space is depicted in Fig. 1a, where the symbol  $\Delta$  stands for the correlated quantity subtracted by the Hartree–Fock quantity. The difference,  $\Delta\bar{H}(v)$ , is positive at  $0 < v < 1.08$  and  $1.94 < v < 4.82$ , whereas it is negative at  $1.08 < v < 1.94$  and  $v > 4.82$ . The predominant contribution of the electron correlation is the density shift from a large- $v$  to a small- $v$  region, in accord with the change in  $\langle v^n \rangle$  discussed

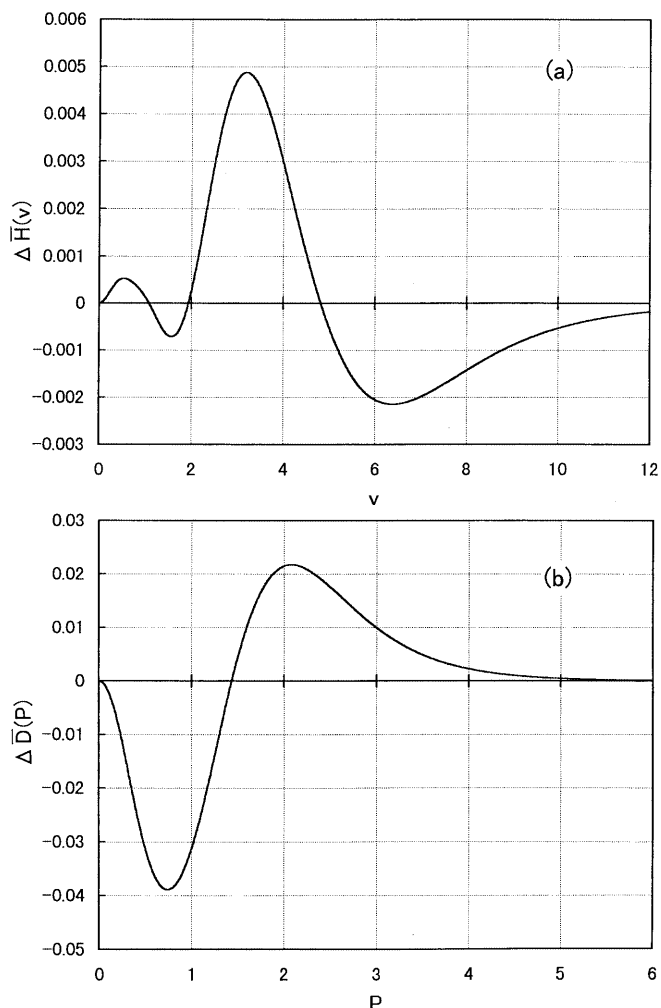
earlier. An analysis by Banyard and coworkers [29, 30], based on a slightly less accurate wave function, shows that the major feature in  $\Delta\bar{H}(v)$  is due to the two electrons in the  $1s$  subshell, and the electron correlation effect mainly works to reduce the distance of the innermost electrons in momentum space.

On the other hand, Table 2 shows that the electron correlation decreases the extracule moments  $\langle P^n \rangle$  with  $n < 0$  and increases  $\langle P^n \rangle$  with  $n > 0$ . These changes are also found in the  $\langle P^n \rangle$  values reported previously by Gálvez et al. [20]. The correlation effect,  $\Delta\bar{D}(P)$ , on the extracule density,  $\bar{D}(P)$  is plotted in Fig. 1b, which shows that the extracule density migrates from a small- $P$  ( $0 < P < 1.43$ ) to a large- $P$  ( $P > 1.43$ ) region, when the electron correlation is incorporated. Thus, two electrons are less likely to have opposite momenta and the center-of-mass radius of an electron pair in momentum space is larger than the case of the Hartree–Fock approximation. The results are consistent with the correlation effect observed in the extracule moments,  $\langle P^n \rangle$ . The correlation effect,  $\Delta\bar{D}(P)$ , was also shown by Gálvez et al. [20] as a function of  $P$ , but the plot is erratic because their  $\Delta\bar{D}(P)$  integrated over  $(0, \infty)$  is clearly negative. The integral should vanish in all cases, since both the correlated and the Hartree–Fock  $\bar{D}(P)$  are normalized to the number of electron pairs.

Table 2 also lists the inner product,  $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ , the first moment  $S(+1)$  of the dipole oscillator strength density [26, 27], and the momentum-space statistical angular correlation coefficient,  $\tau[\mathbf{p}]$  [28]. The present MCHF values agree well with the most accurate literature values of Yan and Drake [16] (see also Ref. [17]), whenever available. When the consistency of the momentum-space

**Table 2.** Electron-pair properties of the Li atom in momentum space

	Hartree–Fock	Correlated			
	[9, 10]	Sarsa et al.	Banyard and	Present	Yan and Drake
		[19, 20]	Youngman [29]		[16, 17]
Energies					
E	-7.43273	-7.4738	-7.47710	-7.47723	-7.47806
-E/T	1.00000	0.99957	1.00453	1.00000	1.00000
Intracule moments					
$\langle v^{-2} \rangle$	1.46828	1.4633	–	1.47131	–
$\langle v^{-1} \rangle$	1.63450	1.628	1.63705	1.63644	–
$\langle v \rangle$	7.96317	7.945	7.9032	7.92672	–
$\langle v^2 \rangle$	29.7309	29.367	29.1185	29.2998	–
$\langle v^3 \rangle$	160	156	–	155	–
Extracule moments					
$\langle P^{-2} \rangle$	5.87314	5.753	–	5.75272	–
$\langle P^{-1} \rangle$	3.26900	3.235	–	3.23110	–
$\langle P \rangle$	3.98158	4.028	–	4.03731	–
$\langle P^2 \rangle$	7.43273	7.6139	–	7.62950	–
$\langle P^3 \rangle$	20.0	20.80	–	20.6	–
Other two-electron properties					
$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$	0	0.285	0.3277	0.3046	0.3018
$S(+1)$	9.9103	–	–	10.3757	10.3732
$\tau[\mathbf{p}]$	0	–	–	0.0204	–
Sum-rule check					
$\langle p^2 \rangle$	14.8655	14.954	14.8868	14.9545	14.9561
$\delta_{\text{mom}}$	0.0000	0.007	–	0.0000	–



**Fig. 1a,b.** The electron correlation effect on the electron-pair densities of the Li atom in momentum space. (a) Intracule density. (b) Extracule density

intracule and extracule properties is checked by means of  $\delta_{\text{mom}}$  (Eq. 6), we find that  $\delta_{\text{mom}}$  is zero for the present results, whereas it is nonzero for the results of Sarsa et al. [19, 20].

#### 4 Summary

For the Li atom, correlated electron-pair intracule (relative motion) and extracule (center-of-mass motion) properties in momentum space have been reported in an accurate, yet consistent, manner.

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