Interelectronic angles of group 14, 15, and 16 atoms in their low-lying multiplet states

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The average interelectronic angles $\langle \theta_{12} \rangle$ in position space and $\langle \bar{\theta}_{12} \rangle$ in momentum space are examined for the multiplet states arising from the ground electronic configurations of the group 14, 15, and 16 atoms. The angles $\langle \theta_{12} \rangle$ and $\langle \bar{\theta}_{12} \rangle$ are greater than 90 degrees with no exceptions and two electron vectors prefer inverse directions to the same direction on average. Common to all 15 atoms, it is found that in position space, lower multiplets have larger interelectronic angles $\langle \theta_{12} \rangle$ than higher multiplets. However, the opposite is true in momentum space and the interelectronic angles $\langle \bar{\theta}_{12} \rangle$ are smaller in lower multiplets. The differences in the angles $\Delta \langle \theta_{12} \rangle$ and $\Delta \langle \bar{\theta}_{12} \rangle$ between multiplets have good linear correlations with the relative stability ΔE of the multiplets. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605937]

In connection to Hund's empirical rules (see, e.g., Ref. 1) for the relative stability of atomic multiplets, the characteristics of the multiplet states arising from p^2, p^3, and p^4 electronic configurations of group 14, 15, and 16 atoms in the periodic table were extensively studied and discussed in the literature. Good reviews and relevant references are found in Refs. 2–7. The properties examined in the literature include the electron–nucleus attraction energy $V_{ne} = \langle -Z/r \rangle$, the electron–electron repulsion energy $V_{ee} = \langle 1/r_{12} \rangle$, the electron kinetic energy $\langle p^2/2 \rangle$, the average electron–nucleus radius $\langle r \rangle$, the electron-pair intracule (relative motion) $\langle r_{12}^n \rangle$ and extracule (center-of-mass motion) $\langle R_{12}^n \rangle$ moments in position space, the corresponding moments $\langle p_{12}^n \rangle$ and $\langle P_{12}^n \rangle$ in momentum space, and some of their parent density functions. All these quantities are functions of one- and two-electron *distances* either in position or momentum space. In the present paper, we report another aspect of the multiplet states in p^2, p^3, and p^4 configurations based on the study of the interelectronic *angles* $\langle \theta_{12} \rangle$ in position space and $\langle \bar{\theta}_{12} \rangle$ in momentum space.

For an N-electron ($N \geq 2$) system, the average interelectronic angle $\langle \theta_{12} \rangle$ in position space is defined[8] by

$$\langle \theta_{12} \rangle = \frac{2}{N(N-1)} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \theta_{ij} \right\rangle, \qquad (1)$$

where the large angle brackets $\langle \ \rangle$ on the right-hand side stand for the expectation value over the wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ with $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ being the combined position-spin coordinates of the electron i and θ_{ij} ($0 \leq \theta_{ij} \leq \pi$) is the angle spanned by the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$. The interelectronic angle $\langle \bar{\theta}_{12} \rangle$ in momentum space is defined[9] analogously and represents the average angle between any two electron momentum vectors $\mathbf{p}_i$ and $\mathbf{p}_j$.

For the ^3P, ^1D, and ^1S multiplets of five group 14 atoms (C, Si, Ge, Sn, Pb) with p^2 configurations, the ^4S, ^2D, and ^2P multiplets of five group 15 atoms (N, P, As, Sb, Bi) with p^3 configurations, and the ^3P, ^1D, and ^1S multiplets of five group 16 atoms (O, S, Se, Te, Po) with p^4 configurations, the

average angles $\langle \theta_{12} \rangle$ and $\langle \bar{\theta}_{12} \rangle$ were calculated from numerical Hartree–Fock wave functions based on the procedures developed recently in Refs. 8 and 9. Heavy atoms such as Pb (atomic number $Z = 82$), Bi ($Z = 83$), and Po ($Z = 84$) were included in this study to see whether the difference in the angles between different multiplets is common throughout a group of the periodic table.

Table I summarizes the interelectronic angles $\langle \theta_{12} \rangle$ in position space for the 15 atoms. We first find that in all the cases, $\langle \theta_{12} \rangle$ are greater than 90 degrees and two electrons are more likely to be on opposite sides of the nucleus than on the same side, though the angle gradually decreases as atomic number Z increases. An important observation in Table I is that a lower multiplet has a larger interelectronic angle $\langle \theta_{12} \rangle$ than a higher multiplet with no exceptions. It is known in the literature[6,10] that a lower multiplet has more tight density distribution around the nucleus than a higher multiplet, which results in a smaller V_{ne} and a larger V_{ee} of the lower multiplet. Thus a larger interelectronic angle $\langle \theta_{12} \rangle$ does not correspond to a smaller interelectronic repulsion energy V_{ee}. The results are interpreted that though lower multiplets have larger V_{ee}, they still try to reduce V_{ee} by increasing $\langle \theta_{12} \rangle$. The differences $\Delta \langle \theta_{12} \rangle$ of the angles relative to the ground multiplet have good negative linear correlations $\Delta \langle \theta_{12} \rangle \cong a \Delta E + b$ with the corresponding total energy differences ΔE between the multiplets, though the constants a (<0) and b (≈ 0) differ from one atom to another. As shown in Table I, the correlation coefficients (CCs) are smaller than -0.999 in many cases. The worst is -0.995 for the C atom. For the group 14 and 16 atoms, the ratio $\Delta E(^1S - {}^3P)/\Delta E(^1D - {}^3P)$ of the two energy differences is 5/2, while for the group 15 atoms the ratio $\Delta E(^2P - {}^4S)/\Delta E(^2D - {}^4S)$ is 5/3 in the frozen orbital approximation.[7,11–13] The Hartree–Fock ratios were calculated[6] to be about 2.43, 1.65, and 2.48 for the group 14, 15, and 16 atoms, respectively. In Table I, the corresponding ratios in the angular differences are rather close to these values.

The average interelectronic angles $\langle \bar{\theta}_{12} \rangle$ in momentum

TABLE I. Interelectronic angles $\langle \theta_{12} \rangle$ (in degrees) in position space. CC denotes the correlation coefficient between $\Delta \langle \theta_{12} \rangle$ and ΔE.

Group 14 atom	^3P	^1D	^1S	$(^1S - {}^3P)/(^1D - {}^3P)$	CC
C ($Z=6$)	92.9518	92.9210	92.8577	3.059	−0.995 381
Si ($Z=14$)	91.9367	91.9288	91.9145	2.799	−0.998 145
Ge ($Z=32$)	91.2000	91.1984	91.1955	2.765	−0.998 424
Sn ($Z=50$)	90.8304	90.8298	90.8287	2.792	−0.998 244
Pb ($Z=82$)	90.5717	90.5715	90.5711	2.793	−0.998 258
Group 15 atom	^4S	^2D	^2P	$(^2P - {}^4S)/(^2D - {}^4S)$	CC
N ($Z=7$)	93.1726	93.1493	93.1303	1.815	−0.998 003
P ($Z=15$)	91.8900	91.8829	91.8776	1.746	−0.999 302
As ($Z=33$)	91.1746	91.1730	91.1718	1.738	−0.999 412
Sb ($Z=51$)	90.8183	90.8177	90.8173	1.744	−0.999 338
Bi ($Z=83$)	90.5660	90.5658	90.5656	1.744	−0.999 343
Group 16 atom	^3P	^1D	^1S	$(^1S - {}^3P)/(^1D - {}^3P)$	CC
O ($Z=8$)	93.1548	93.1436	93.1248	2.690	−0.999 329
S ($Z=16$)	91.8327	91.8292	91.8236	2.617	−0.999 705
Se ($Z=34$)	91.1469	91.1460	91.1447	2.607	−0.999 745
Te ($Z=52$)	90.8052	90.8049	90.8044	2.617	−0.999 710
Po ($Z=84$)	90.5599	90.5597	90.5595	2.617	−0.999 710

space are listed in Table II for the 15 atoms in the groups 14, 15, and 16. As was the case in position space, the angles $\langle \bar{\theta}_{12} \rangle$ are always larger than 90 degrees and the momentum vectors $\mathbf{p}_i$ and $\mathbf{p}_j$ of two electrons prefer opposite directions. We find in the table that in every atom, the momentum-space interelectronic angle $\langle \bar{\theta}_{12} \rangle$ is smaller in a lower multiplet than in a higher multiplet. At present, we do not have any physical interpretation which explains the change in angles $\langle \bar{\theta}_{12} \rangle$ in relation to the relative stability of the multiplets. When the differences in the angles and total energies relative to the ground multiplet are examined, however, we observe excellent positive linear correlations between them, $\Delta \langle \bar{\theta}_{12} \rangle \cong \bar{a} \Delta E + \bar{b}$, where the constants $\bar{a}$ (>0) and $\bar{b}$ (≈ 0) differ from an atom to another. As given in Table II, the CCs be-

tween $\Delta \langle \bar{\theta}_{12} \rangle$ and ΔE are greater than 0.999 in all the cases. In Table II, we also find that the ratios between the two angular differences in momentum space are again close to the constants 5/2 (group 14 and 16 atoms) and 5/3 (group 15 atoms).

The two linear correlations observed above between $\Delta \langle \theta_{12} \rangle$ and ΔE and between $\Delta \langle \bar{\theta}_{12} \rangle$ and ΔE suggest a direct connection between the angular differences $\Delta \langle \theta_{12} \rangle$ in position space and $\Delta \langle \bar{\theta}_{12} \rangle$ in momentum space. Numerical examinations show the anticipation is true; for all the 15 atoms, $\Delta \langle \theta_{12} \rangle$ and $\Delta \langle \bar{\theta}_{12} \rangle$ (or $\langle \theta_{12} \rangle$ and $\langle \bar{\theta}_{12} \rangle$) have negative linear correlations. The CCs range from −0.995 to −1.000.

In summary, we have shown that for the group 14, 15, and 16 atoms in their ground electronic configurations, a

TABLE II. Interelectronic angles $\langle \bar{\theta}_{12} \rangle$ (in degrees) in momentum space. CC denotes the correlation coefficient between $\Delta \langle \bar{\theta}_{12} \rangle$ and ΔE.

Group 14 atom	^3P	^1D	^1S	$(^1S - {}^3P)/(^1D - {}^3P)$	CC
C ($Z=6$)	92.6327	92.6879	92.7661	2.416	0.999 998
Si ($Z=14$)	91.7639	91.7727	91.7850	2.383	0.999 950
Ge ($Z=32$)	91.1506	91.1521	91.1542	2.351	0.999 870
Sn ($Z=50$)	90.7950	90.7956	90.7965	2.405	0.999 981
Pb ($Z=82$)	90.5530	90.5533	90.5536	2.416	0.999 991
Group 15 atom	^4S	^2D	^2P	$(^2P - {}^4S)/(^2D - {}^4S)$	CC
N ($Z=7$)	92.8181	92.8660	92.8972	1.651	1.000 000
P ($Z=15$)	91.7101	91.7198	91.7262	1.650	1.000 000
As ($Z=33$)	91.1155	91.1173	91.1185	1.647	0.999 998
Sb ($Z=51$)	90.7780	90.7788	90.7793	1.657	0.999 998
Bi ($Z=83$)	90.5450	90.5453	90.5455	1.659	0.999 996
Group 16 atom	^3P	^1D	^1S	$(^1S - {}^3P)/(^1D - {}^3P)$	CC
O ($Z=8$)	92.8690	92.8886	92.9175	2.467	0.999 999
S ($Z=16$)	91.6656	91.6704	91.6775	2.474	1.000 000
Se ($Z=34$)	91.0846	91.0856	91.0870	2.473	0.999 999
Te ($Z=52$)	90.7627	90.7631	90.7638	2.486	0.999 999
Po ($Z=84$)	90.5376	90.5377	90.5379	2.490	0.999 998

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lower multiplet of an atom has a larger $\langle \theta_{12} \rangle$ and a smaller $\langle \bar{\theta}_{12} \rangle$ than a higher multiplet. The differences in the inter-electronic angles $\Delta \langle \theta_{12} \rangle$ in position space and $\Delta \langle \bar{\theta}_{12} \rangle$ in momentum space have good linear correlations with the relative stability ΔE of the multiplets. Linear correlations between $\Delta \langle \theta_{12} \rangle$ and $\Delta \langle \bar{\theta}_{12} \rangle$ have also been observed for all the atoms. Preliminary examinations of the ground multiplets of light atoms by multiconfiguration Hartree–Fock calculations show that the inclusion of the electron correlation increases $\langle \theta_{12} \rangle$ by 1.4, 0.9, and 0.6 degrees, while decreases $\langle \bar{\theta}_{12} \rangle$ by 1.0, 0.7, and 0.5 degrees, respectively, for the C, N, and O atoms. We wish to report whether the present observation at the Hartree–Fock level remain unchanged at the correlated level, when correlated data are available in a systematic manner.

[1] I. N. Levine, *Quantum Chemistry*, 5th ed. (Prentice Hall, Upper Saddle River, NJ, 2000), p. 328.

[2] R. L. Snow and J. L. Bills, J. Chem. Educ. **51**, 585 (1974).

[3] J. Katriel and R. Pauncz, Adv. Quantum Chem. **10**, 143 (1977).

[4] R. J. Boyd, Nature (London) **310**, 480 (1984).

[5] W. Kutzelnigg and J. D. Morgan III, Z. Phys. D: At., Mol. Clusters **36**, 197 (1996).

[6] T. Koga, H. Matsuyama, J. S. Dehesa, and A. J. Thakkar, J. Chem. Phys. **110**, 5763 (1999).

[7] T. Koga and H. Matsuyama, J. Chem. Phys. **111**, 643 (1999).

[8] T. Koga, J. Chem. Phys. **117**, 10493 (2002).

[9] T. Koga, Theor. Chem. Acc. (in press).

[10] T. Koga and Y. Koshida, J. Chem. Phys. **111**, 54 (1999).

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970).

[12] J. P. Colpa, Mol. Phys. **28**, 581 (1974).

[13] J. P. Colpa, A. J. Thakkar, V. H. Smith, Jr., and P. Randle, Mol. Phys. **29**, 1861 (1975).