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Relative sizes of atoms observed in electron momentum densities

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The radial electron momentum densities $I(p)$ of atoms are known to reveal several local maxima and minima. For the 103 atoms from H to Lr in their ground states, we report that the reciprocal momenta $1/p_{\max}$ and $1/p_{\min}$, where p_{\max} and p_{\min} are the locations of the maxima and minima in $I(p)$, respectively, have good linear correlations with the relative sizes R of atoms, defined based on the spherically averaged densities $\rho(r)$ in position space. © 2002 American Institute of Physics. [DOI: 10.1063/1.1463445]

I. INTRODUCTION

The radial electron momentum density $I(p)$ is defined by

$$I(p) \equiv \sum_{i=1}^N \langle \delta(p - |\mathbf{p}_i|) \rangle, \quad (1)$$

where $\delta(x)$ is the one-dimensional Dirac delta function and the brackets $\langle \rangle$ stand for the expectation value over an N -electron momentum wave function $\Phi(\mathbf{y}_1, \dots, \mathbf{y}_N)$ with $\mathbf{y}_i \equiv (\mathbf{p}_i, \sigma_i)$ being the combined momentum-spin coordinates of the i th electron. The momentum density $I(p)$ represents the probability density function for the momentum magnitude $|\mathbf{p}_i|$ of any electrons i to be p , and is normalized to N , the number of electrons. It is important that the density $I(p)$ is intimately related with experimental measurements: Within the impulse approximation, the isotropic Compton profile $J(q)$ is given¹ in terms of $I(p)$ by

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} dp p^{-1} I(p), \quad (2)$$

which conversely implies $I(p) = -2p[dJ(p)/dp]$.

Moreover, many physical properties are connected¹⁻⁶ to the momentum moments $\langle p^n \rangle$ defined by

$$\langle p^n \rangle \equiv \int_0^{\infty} dp p^n I(p). \quad (3)$$

Examples are: $\langle p^{-1} \rangle$ is twice the Compton peak height $J(0)$, $\langle p \rangle / \pi$ is close⁷ to the Slater-Dirac exchange energy, $\langle p^2 \rangle$ is twice the nonrelativistic electronic kinetic energy, $\langle p^3 \rangle$ is approximately proportional^{7,8} to the initial value of the Patterson function in x-ray crystallography, and $\langle p^4 \rangle$ determines⁹ the Breit-Pauli mass-velocity correction in quasirelativistic quantum theory.

In addition to the above important characteristics, the momentum densities $I(p)$ of atoms are known¹⁰⁻¹⁴ to have several local maxima and minima. In the present article, we point out that for the 103 neutral atoms H through Lr in their ground states, the momenta p_{\max} and p_{\min} , where the maxima and minima are observed in $I(p)$, are related with

the relative sizes R of atoms, which are derived^{15,16} from the analysis of the electron density $\rho(r)$ in position space. Hartree atomic units are used throughout.

II. RELATIVE SIZES OF ATOMS

Together with the additivity assumption for molecules and solids, various sizes were introduced¹⁷ empirically for atoms and ions, such as covalent, ionic, and metallic radii. To define intrinsic radii of atoms, before influenced by the molecular environment, Boyd¹⁵ examined several quantities derived from the spherically averaged density $\rho(r)$ in position space

$$\rho(r) \equiv (4\pi r^2)^{-1} \sum_{i=1}^N \langle \delta(r - |\mathbf{r}_i|) \rangle, \quad (4)$$

and found that a density contour approach given by

$$\rho(R) = C, \quad (5)$$

yields the most appropriate result for the relative sizes R of atoms, where C is a constant common to all the atoms considered. Boyd used¹⁵ $C = 1 \times 10^{-4}$ for the 54 atoms from H (atomic number $Z=1$) to Xe ($Z=54$), but a smaller value such as $C = 5 \times 10^{-5}$ was suggested later¹⁶ when the 103 atoms H through Lr ($Z=103$) were examined. Since the calculated relative radii R are substantially larger than the empirical radii due to the small value of C , scaling procedures were further introduced,^{15,16} which scale the theoretical radii R down to values \bar{R} with the magnitude of the empirical radii, referring to the univalent radii¹⁷ of Pauling for the first five rare-gas atoms. In the following discussion on the locations of the maxima and minima in the electron momentum density, however, we refer to the original radii R obtained from the numerical Hartree-Fock densities¹⁸ $\rho(r)$ with $C = 5 \times 10^{-5}$ as the relative sizes of atoms, since the two sets of values R and \bar{R} have parallel behavior against Z .

III. LOCAL MAXIMA AND MINIMA IN RADIAL MOMENTUM DENSITIES

For atomic systems, the presence of several local maxima and minima in the radial momentum densities $I(p)$ was reported in the literature,¹⁰⁻¹⁴ where we do not consider

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the two trivial local minima at $p=0$ and ∞ . Among them, the study of Simas *et al.*,¹⁴ which covers the 92 atoms from H to U, appears to be most extensive. These authors clarified¹⁴ that the local maxima and minima in $I(p)$ are manifestation of outer electronic shells and intershell boundaries, respectively, in atoms.

Since all these studies are based on approximate Roothaan–Hartree–Fock wave functions, we have first reexamined the extremum characteristics of $I(p)$ using the numerical Hartree–Fock wave functions¹⁹ for the 103 atoms H through Lr in their experimental ground states.^{20,21} Fortunately, the previous observations remain unaltered. Based on the decomposition of $I(p)$ into shell contributions, we have also confirmed that the local maxima in $I(p)$ originate from outer electronic shells. The numbers of local maxima in the Hartree–Fock $I(p)$ of the 103 atoms are summarized as follows:

- (i) Seven atoms with $Z=1, 2, 6-10$ have a single maximum;
- (ii) 35 atoms with $Z=3-5, 11-18, 21-36, 46, 48-54$ have two local maxima;
- (iii) 48 atoms with $Z=19, 20, 37-45, 47, 55-86, 100-103$ have three local maxima;
- (iv) 13 atoms with $Z=87-99$ have four local maxima.

Except for the case (i), there are local minima between two successive local maxima. Thus the number of local minima is less than the number of local maxima by one in every atom.

The correspondence between the local maxima in $I(p)$ and the outer electronic shells suggests that the locations p_{\max} of these maxima would have some definite relations with the relative size R of atoms, because the outer shells also give a significant contribution to the tail region of $\rho(r)$ from which R is defined. The smallest (or first) p_{\max} , corresponding to the outermost shell, is our first candidate for the anticipated correlation. Moreover, we expect a positive correlation between the reciprocal momenta $1/p_{\max}$ and the relative sizes R , since the position and momentum representations emphasize inverse regions of the respective spaces.

The correlation between the reciprocals of the first p_{\max} and the relative sizes R is plotted in Fig. 1(a) for the 103 atoms from H to Lr. We observe that $1/p_{\max}$ and R are positively correlated, but the relation is not clear when the 103 atoms are considered all together. In fact, the correlation coefficient (CC) is only 0.935 for a linear regression in the form of

$$1/p_{\max} \cong aR + b, \quad (6)$$

where a and b are least square parameters. However, we find a good correlation between $1/p_{\max}$ and R , if the 103 atoms are separated into three groups based on the numbers of electrons in the outermost s and p subshells; 16 atoms with s^1 configurations, 56 atoms with s^2 configurations, and 30 atoms with s^2p^k ($k=1-6$) configurations. (We treated the Pd atom ($Z=46$) as a sole exception, since it lies in the fifth period in spite of the vacant d shell.) Figure 1(a) shows that there is a good linear correlation between $1/p_{\max}$ and R of the atoms in each group. The CCs in the regression analysis [Eq.

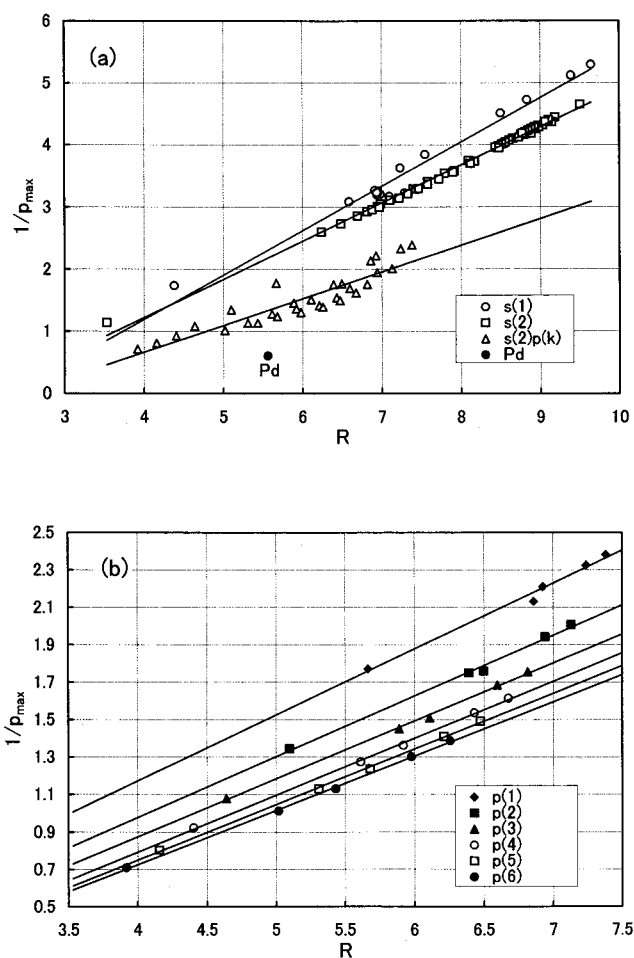


FIG. 1. Correlation between the reciprocals of the first p_{\max} and the relative sizes R . (a) 103 atoms H through Lr. (b) 30 atoms with the outermost s^2p^k ($k=1-6$) configurations.

(6)] are now 0.987, 0.998, and 0.913 for the three groups, respectively, as summarized in Table I. The poorest correlation for the atoms with s^2p^k configurations is improved, when the group is further decomposed into six subgroups on the basis of the number k of the p electrons. The results are summarized in Fig. 1(b) and Table I; the CCs are never smaller than 0.993. We thus conclude that the locations p_{\max} of the first maxima in the electron momentum densities $I(p)$

TABLE I. Linear correlation between the reciprocal first p_{\max} and R .

Outermost sp configuration	Number of atoms	a	b	CC
All	103	0.810 103	-2.916 880	0.935 090
s^1	16	0.715 001	-1.674 131	0.986 557
s^2	56	0.615 120	-1.244 998	0.997 703
s^2p^k ($k=1-6$)	30 ^a	0.430 253	-1.062 814	0.913 300
s^2p^1	5	0.352 493	-0.237 610	0.993 484
s^2p^2	5	0.324 216	-0.319 457	0.997 717
s^2p^3	5	0.309 095	-0.361 931	0.998 951
s^2p^4	5	0.303 583	-0.421 738	0.999 257
s^2p^5	5	0.296 491	-0.436 294	0.999 427
s^2p^6	5 ^a	0.289 660	-0.433 062	0.999 521

^aThe Pd atom is excluded.

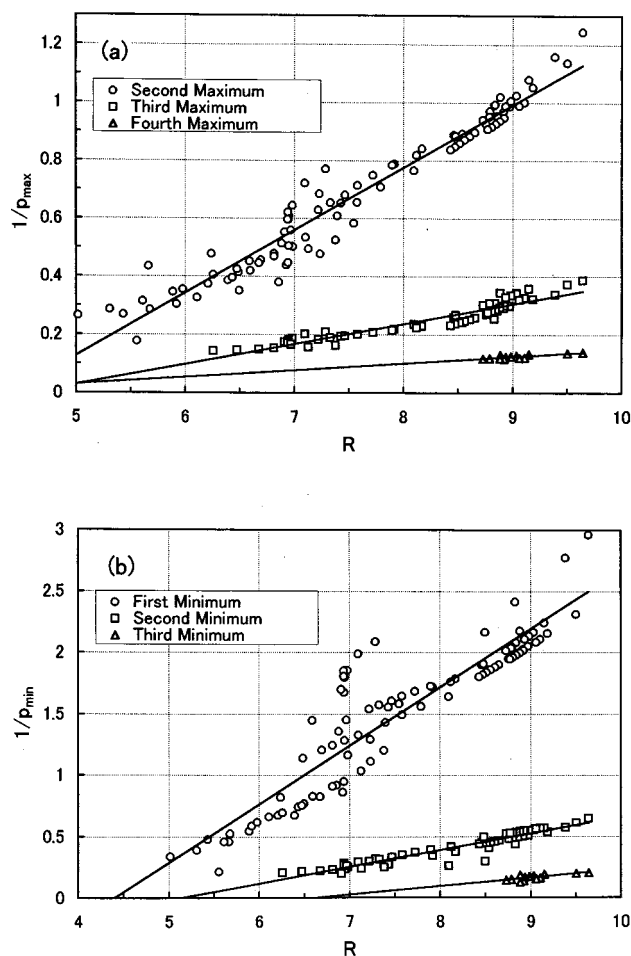


FIG. 2. Correlation between the reciprocals of p_{\max} or p_{\min} and the relative sizes R . (a) $1/p_{\max}$ and R . (b) $1/p_{\min}$ and R .

are connected with the relative sizes R of atoms, if the difference in the numbers of the outermost s and p electrons is taken into account.

The classification of the $1/p_{\max}$ – R correlation based on the outermost sp configurations can be rationalized as follows. The numerical values of the first p_{\max} are smaller than unity in most atoms, and are governed by the momentum densities $I(p)$ in their small p regions. Moreover, the small- p asymptotic behavior of the subshell momentum density $I_{nl}(p)$, specified by the principal n and azimuthal l quantum numbers, is known¹⁹ to be

$$I_{nl}(p) = A_{nl}p^{2l+2} + B_{nl}p^{2l+4} + O(p^{2l+6}), \quad (7)$$

where A_{nl} and B_{nl} are constants, which include the $(2l)$ th and $(2l+2)$ th derivatives at $p=0$ of the spherically averaged density $\Pi_{nl}(p) = I_{nl}(p)/(4\pi p^2)$, respectively. Equation (7) clarifies that the leading p^2 and p^4 terms, arising from the outermost s ($l=0$) and p ($l=1$) subshells, give the predominant contribution to the value of the first p_{\max} .

Above the correlation between the reciprocal momenta $1/p_{\max}$ of the first maxima in $I(p)$ and the relative sizes R has been discussed. We have also examined the possibility of the correlation between R and $1/p_{\max}$ of the second, third, and fourth maxima, though all the 103 atoms do not always

TABLE II. Linear correlations between $1/p_{\max}$ and R and between $1/p_{\min}$ and R .

Extremum	Number of atoms	a	b	CC
Maximum				
First	103	0.810 103	−2.916 880	0.935 090
Second	96	0.216 273	−0.954 456	0.974 050
Third	61	0.068 905	−0.315 087	0.944 805
Fourth	13	0.023 519	−0.087 281	0.831 485
Minimum				
First	96	0.476 119	−2.092 869	0.917 366
Second	61	0.135 641	−0.696 451	0.950 843
Third	13	0.068 291	−0.453 771	0.742 036

have these maxima. A positive linear correlation is again observed as summarized in Fig. 2(a) and Table II. For the second and third maxima in $I(p)$, the CCs (0.974 and 0.945, respectively) are larger than the first, and the reciprocal momenta of these maxima, due to the electrons in the second and third outermost shells, also reflect the relative sizes of atoms. However, the correlation is poorer for the fourth maxima, as the CC value (0.831) shows.

From the observed correlation between $1/p_{\max}$ and R , we further anticipate a positive correlation between $1/p_{\min}$ and R

$$1/p_{\min} \cong aR + b, \quad (8)$$

where p_{\min} is the locations of the minima in the momentum densities $I(p)$. As plotted in Fig. 2(b), our anticipation is found to be correct. The values of CCs given in Table II show that for the first and second minima, the degree of correlation is analogous to that of the maxima, but it is poor for the third minimum.

IV. SUMMARY

For the 103 atoms from H to Lr in their ground states, we have shown that the reciprocal momenta $1/p_{\max}$ and $1/p_{\min}$ have good linear correlations with the relative sizes R of atoms, where p_{\max} and p_{\min} are the locations of the maxima and minima in the radial electron momentum densities $I(p)$, respectively.

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