Electron-pair radii and relative sizes of atoms

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The electron-pair intracule (relative motion) $h(u)$ and extracule (center-of-mass motion) $d(R)$ densities represent probability densities for the interelectronic distance and the center-of-mass radius of any pairs of electrons, respectively. For 102 atoms from He (atomic number $Z=2$) to Lr ($Z=103$), we report that electron-pair radii R_{2i} and R_{2e}, defined by $h(R_{2i})=c_{2i}$ and $d(R_{2e})=c_{2e}$, have good linear correlations with the relative sizes R_1 of atoms introduced based on the single-electron density $\rho(r)$ such that $\rho(R_1)=c_1$, where c_1, c_{2i}, and c_{2e} are constants common to the 102 atoms. It is also shown that an interesting relation $R_{2e}\cong R_{2i}/2$ holds, if c_{2e} is set equal to $8c_{2i}$. © *2000 American Institute of Physics.* [S0021-9606(00)30316-6]

I. INTRODUCTION AND DEFINITIONS

The motion of an electron pair in atoms is characterized[1–3] by the spherically averaged intracule (relative motion) density $h(u)$,

$$h(u)\equiv(4\pi u^2)^{-1}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \delta(u-|\mathbf{r}_1-\mathbf{r}_2|)\Gamma(\mathbf{r}_1,\mathbf{r}_2), \quad (1)$$

and by the spherically averaged extracule (center-of-mass motion) density $d(R)$,

$$d(R)\equiv(4\pi R^2)^{-1}\int d\mathbf{r}_1\, d\mathbf{r}_2\, \delta(R-|\mathbf{r}_1+\mathbf{r}_2|/2)\Gamma(\mathbf{r}_1,\mathbf{r}_2), \quad (2)$$

where $\delta(x)$ is the one-dimensional Dirac delta function and

$$\Gamma(\mathbf{r}_1,\mathbf{r}_2)\equiv\frac{N(N-1)}{2}\int d\sigma_1\, d\sigma_2\, d\mathbf{x}_3\cdots d\mathbf{x}_N \times|\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)|^2, \quad (3)$$

is the spin-reduced two-electron density function[4] associated with an N-electron wave function $\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ with $\mathbf{x}_i\equiv(\mathbf{r}_i,\sigma_i)$ being the combined position-spin coordinates of the electron i. By the definitions (1)–(3), the densities $h(u)$ and $d(R)$ are normalized as

$$4\pi\int_0^\infty du\, u^2 h(u)=4\pi\int_0^\infty dR\, R^2 d(R)=N(N-1)/2, \quad (4)$$

where $N(N-1)/2$ is the number of electron pairs in the system.

The intracule density $h(u)$ represents[1–3] the probability density function for the relative distance $|\mathbf{r}_i-\mathbf{r}_j|$ of any pair of electrons i and j to be u. It has been used in several physical and chemical contexts particularly in relation to the electron correlation problem (see references given in Refs. 2, 3, and 5–8). On the other hand, the extracule density $d(R)$ represents[1–3] the probability density function for the center-of-mass radius $|\mathbf{r}_i+\mathbf{r}_j|/2$ of any pair of electrons i and j to be R. The density was used to study the shell structure in some atoms and bonding characteristics in simple molecules (see references in Refs. 2, 3, and 9–12).

In the literature, many studies, within and beyond the Hartree–Fock theory, were carried out on the electron-pair intracule and extracule densities of light atoms and small molecules, based on approximate basis-set-expansion wave functions (see Refs. 2, 3, and 5–12 and references therein). However, it is rather recently that systematic yet accurate Hartree–Fock electron-pair densities have been obtained[6,7,10,11,13] for the ground-state neutral atoms He ($Z=2$) through Lr ($Z=103$), where Z denotes atomic number. Moreover, various properties of the atomic intracule and extracule densities have been clarified, including their modalities,[7,11,13] Maclaurin expansions,[14] coalescence $h(0)$ and counterbalance $d(0)$ densities,[15,16] and moments $\langle u^n\rangle$ and $\langle R^n\rangle$[6,10,13] defined by

$$\langle u^n\rangle\equiv4\pi\int_0^\infty du\, u^{n+2}h(u), \quad (5a)$$

$$\langle R^n\rangle\equiv4\pi\int_0^\infty dR\, R^{n+2}d(R). \quad (5b)$$

Though the relative motion and the center-of-mass motion of two particles are completely independent, it has been pointed out[10,11,17] that the Coulombic binding of electrons in an atomic system generates approximate isomorphic relations between the intracule and extracule properties. Two interesting and important examples are[10,11,17]

$$d(R)\cong8h(2R), \quad (6a)$$

$$\langle u^n\rangle/\langle R^n\rangle\cong2^n. \quad (6b)$$

Approximate linear correlations of the two-electron moments $\langle u^n\rangle$ and $\langle R^n\rangle$ with the one-electron moments $\langle r^n\rangle$ have also been reported,[18] where

$$\langle r^n\rangle\equiv4\pi\int_0^\infty dr\, r^{n+2}\rho(r), \quad (7)$$

in which the spherically averaged single-electron density $\rho(r)$ is defined by

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$$\rho(r) \equiv N(4\pi r^2)^{-1} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \times \delta(r - |\mathbf{r}_1|) |\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 = \frac{2}{N-1} (4\pi r^2)^{-1} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \delta(r - |\mathbf{r}_1|) \Gamma(\mathbf{r}_1, \mathbf{r}_2). \tag{8}$$

In the present paper, we study the radii R_{2i} and R_{2e} of the intracule $h(u)$ and extracule $d(R)$ densities specified by a small contour value, i.e.,

$$h(R_{2i}) = c_{2i}, \tag{9a}$$

$$d(R_{2e}) = c_{2e}, \tag{9b}$$

for the 102 atoms He through Lr, where c_{2i} and c_{2e} are constants common to all the atoms. As observed between the two-electron $\langle u^n \rangle$ and $\langle R^n \rangle$ moments and the one-electron $\langle r^n \rangle$ moments, we have expected that the electron-pair radii R_{2i} and R_{2e} would have some relations with the "relative sizes of atoms" R_1 defined by Boyd[19] as

$$\rho(R_1) = c_1, \tag{10}$$

based on choosing an appropriate contour value c_1 in the single-electron density function $\rho(r)$. In the next section, Boyd's relative sizes of atoms are outlined and a modification is mentioned. In Sec. III, the electron-pair radii R_{2i} and R_{2e} are presented and discussed using the intracule and extracule densities from numerical Hartree–Fock calculations. It will be found that our anticipation stated above is true and the radii R_{2i} and R_{2e} have good linear correlations with R_1. We also find that an approximation $R_{2e} \cong R_{2i}/2$ is valid, if we choose the contour values as $c_{2e} = 8c_{2i}$. Hartree atomic units are used, except that numerical values of radii are given in pm with the conversion factor 1 bohr=52.917 7249 pm.[20]

II. RELATIVE SIZES OF ATOMS

Together with an assumed additivity in molecules and solids, various "sizes" were devised[21] empirically for atoms and ions, such as covalent, ionic, van der Waals, metallic, and crystal radii. To define intrinsic radii of atoms, before influenced by the surrounding environment in molecules and solids, Boyd[19] examined several quantities derived from the single-electron density $\rho(r)$, and found that a density contour approach given by Eq. (10) gives the most appropriate measure for the relative sizes of atoms (see also Refs. 22 and 23). Considering 54 atoms from H ($Z=1$) to Xe ($Z=54$) and using the approximate Hartree–Fock density $\rho(r)$ constructed from Clementi wave functions,[24,25] Boyd[19] chose $c_1 = 1 \times 10^{-4}$ so that the following two conditions are satisfied: (i) the atomic radius tends to decrease as Z increases within a period; (ii) the atomic radius tends to increase as Z increases within a group. Since the calculated relative radii are substantially larger than the empirical radii due to the small value of c_1, Boyd[19] further introduced a scaling procedure,

$$\bar{R}_1 = 0.1026 R_1^{1.3234} \quad \text{(in pm)} \tag{11a}$$

which scales the theoretical relative radii R_1 down to $\bar{R}_1$ with the magnitude of the empirical radii, referring to the univalent radii[21] of Pauling for the first five rare-gas atoms.

Since it has been established[26,27] that the wave functions of Clementi *et al.*[24,25] suffer from nontrivial errors and inaccuracies, we have first recalculated the relative sizes of atoms using the numerical Hartree–Fock electron density $\rho(r)$.[28] Fortunately, the errors in the scaled radii $\bar{R}_1$ for the atoms H–Xe have been found to be 1 pm at most except for the seven atoms Cr, Nb, Mo, Ru, Rh, Pd, and Ag, for which an excited state, instead of the ground state,[29,30] was calculated by Clementi[25] and hence by Boyd.[19] For these atoms, the ground-state $\bar{R}_1$ values are 227, 243, 234, 229, 227, 172, and 225 pm in the order given above. In particular, the Pd atom has an exceptionally small radius (172 pm) among the fifth period atoms because of the vacant 5s orbital.

We have next examined whether Boyd's prescription for the relative atomic sizes works also for the heavier atoms Cs ($Z=55$) through Lr ($Z=103$). We have found that the condition (i) is not satisfied when we employ $c_1 = 1 \times 10^{-4}$. For example, the Fr ($Z=87$) and Ra ($Z=88$) atoms were predicted to have $\bar{R}_1 = 338$ and 343 pm, respectively. The problem can be easily resolved if we adopt a smaller value for c_1, though the tendencies imposed in the conditions (i) and (ii) are more emphasized. An example is to use $c_1 = 5 \times 10^{-5}$ together with a linear scaling relation,

$$\bar{R}_1 = 0.7397 R_1 - 43.3699 \quad \text{(in pm)} \tag{11b}$$

which results from a regression analysis of the calculated and empirical univalent radii. We have also examined a regression by a power formula like Eq. (11a), but a linear regression of Eq. (11b) has a better fit. When Eq. (11b) is applied, we have $\bar{R}_1 = 334$ and 329 pm for the Fr and Ra atoms, respectively. To show a systematic trend, the two sets of scaled radii $\bar{R}_1$, determined by $c_1 = 1 \times 10^{-4}$ and 5×10^{-5} in Eq. (10), are exemplified in Table I for the fourth period atoms.

In the next section, the radii R_1 obtained from the contour $c_1 = 5 \times 10^{-5}$ are referred as the relative sizes predicted by the single-electron density in our analysis of the electron-pair radii R_{2i} and R_{2e} for the 102 atoms from He to Lr.

III. RADII OF ELECTRON-PAIR DENSITIES

We have first studied the intracule radii R_{2i} defined by Eq. (9a). The parent intracule densities $h(u)$ were taken from Refs. 6 and 7 for the atoms He through Xe and from Ref. 13 for the atoms Cs through Lr. These densities were constructed by numerical Hartree–Fock calculations in a manner consistent with the single-electron densities employed in the determination of R_1. For the contour value c_{2i}, we have examined seven cases 1×10^{-n} with an integer value of n ranging from 4 to 10. In all the cases, the calculated radii R_{2i} satisfy the conditions (i) and (ii), though the values increase with increasing n. Moreover, the Z dependence of R_{2i} is found to be parallel to that of R_1 for all the c_{2i} values examined. Figure 1 depicts such parallelism for a few selected cases. In fact, we have observed approximate but good linear correlations between the calculated values of R_{2i} and R_1.

TABLE I. Comparison of the relative sizes $\bar{R}_1$, $\bar{R}_{2i}$, and $\bar{R}_{2e}$ for the fourth period atoms.

	$\bar{R}_1$/pm		$\bar{R}_{2i}$/pm	$\bar{R}_{2e}$/pm
Atom	Contour=1×10^{-4} Scaling=Eq. (11a)	5×10^{-5} Eq. (11b)	1×10^{-7} Eq. (12b)	8×10^{-7} Eq. (14c)
K	290	289	302	305
Ca	279	274	277	280
Sc	266	262	266	268
Ti	257	253	258	260
V	249	246	250	252
Cr	227	229	239	241
Mn	236	235	239	241
Fe	229	229	233	235
Co	224	223	228	231
Ni	219	219	224	225
Cu	211	215	229	230
Zn	210	211	216	218
Ga	224	225	243	245
Ge	211	211	216	217
As	196	196	197	197
Se	189	188	189	190
Br	179	179	179	180
Kr	169	169	169	170

For more detailed discussion, we have wished to choose a set of R_{2i} obtained from a particular value of c_{2i}. Since two electrons in an atom can be on opposite sides of the nucleus, we may naively expect that an interelectronic radius

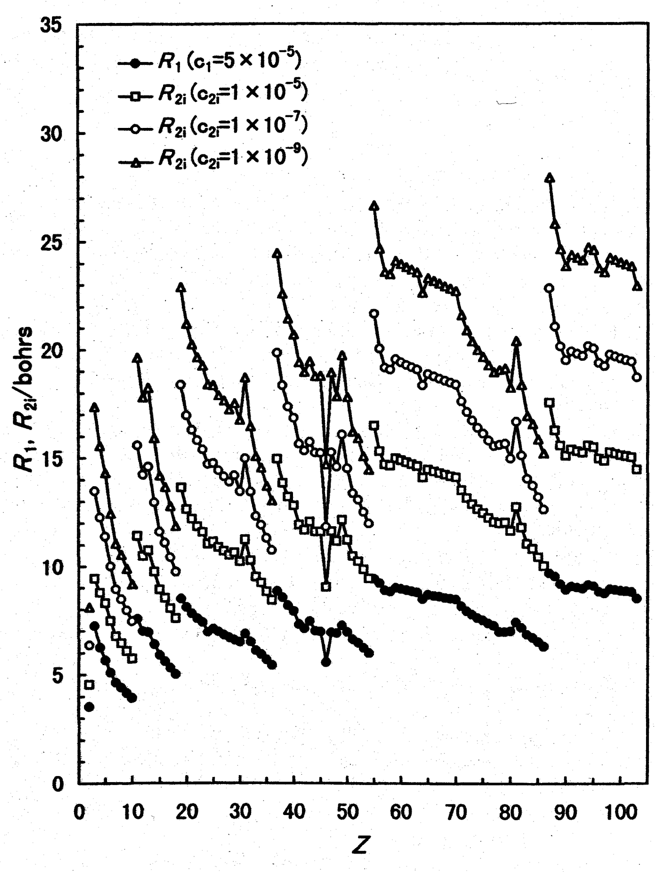

FIG. 1. Z dependence of the relative sizes R_1 and R_{2i} for the 102 atoms from He ($Z=2$) to Lr ($Z=103$).

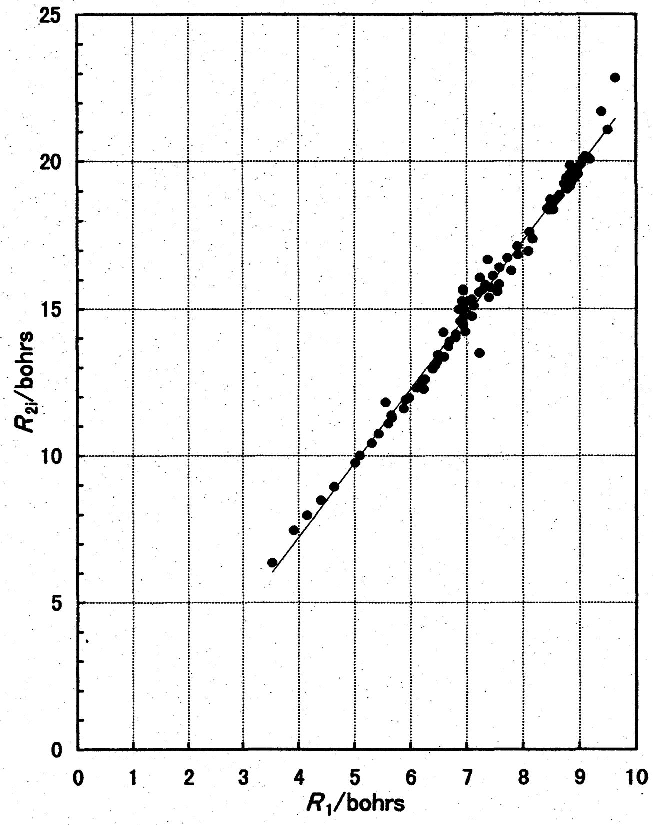

FIG. 2. Correlation between the relative sizes R_1 from $c_1=5\times10^{-5}$ and R_{2i} from $c_{2i}=1\times10^{-7}$ for the 102 atoms.

R_{2i} is approximately twice the electron-nucleus radius R_1. Such a situation is observed when we use $c_{2i}=1\times10^{-7}$ (for $c_1=5\times10^{-5}$); the average of the ratios R_{2i}/R_1 over the 102 atoms is 2.118. For this value of c_{2i}, the correlation between R_{2i} and R_1 is demonstrated in Fig. 2. A regressive analysis shows that the correlation is approximated by

$$R_{2i} \cong 2.5229R_1 - 2.8785, \tag{12a}$$

with a correlation coefficient 0.9932. The result implies that the distribution of the electron-pair intracule density $h(u)$ reflects the relative size of an atom defined from the distribution of the single-electron density $\rho(r)$. If we introduce a linear scaling relation,

$$\bar{R}_{2i} = 0.3278R_{2i} - 16.8285 \quad \text{(in pm)} \tag{12b}$$

based on the comparison of R_{2i} with the empirical univalent radii,[21] the scaled radii $\bar{R}_{2i}$ predict similar sizes as $\bar{R}_1$ for most of the 102 atoms. Table I explicitly compares the $\bar{R}_1$ and $\bar{R}_{2i}$ values for the fourth period atoms K through Kr. The differences between $\bar{R}_1$ and $\bar{R}_{2i}$ are less than 5 pm in most cases. However, $\bar{R}_{2i}$ gives a slightly larger value (10–18 pm) than $\bar{R}_1$ for the four atoms K, Cr, Cu, and Ga, where the outermost $4s$ or $4p$ orbital is singly occupied. An analogous trend is observed for the remaining atoms, and the Fr atom ($Z=87$) with a singly occupied $7s$ orbital has the largest difference 45 pm. The averages of the absolute and relative deviations over the 102 atoms are 11.4 pm and 4.3%, respectively.

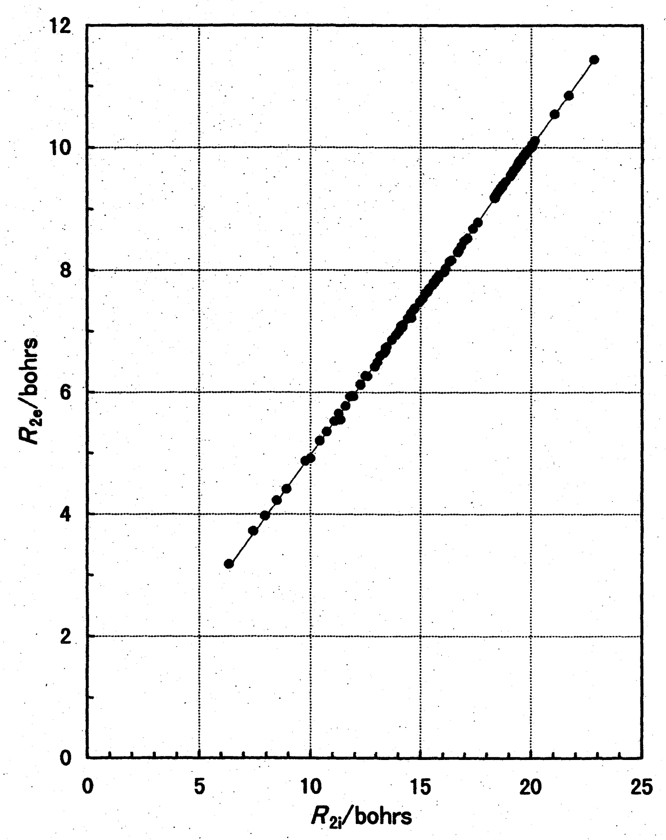

FIG. 3. Correlation between the extracule radius R_{2e} and the intracule radius R_{2i} obtained from $c_{2e}=8c_{2i}=8\times10^{-7}$.

Next we consider the radius R_{2e}, defined by Eq. (9b), of the electron-pair extracule density $d(R)$. Before we perform numerical examinations, a theoretical conjecture can be obtained from the approximate isomorphic relation Eq. (6a). If we assume that Eq. (6a) is valid for a large value of R where both $h(2R)$ and $d(R)$ are small, we have

$$h(R_{2i})\cong\tfrac{1}{8}d(R_{2i}/2), \tag{13a}$$

which means an interesting relation that

$$R_{2e}\cong\tfrac{1}{2}R_{2i}, \tag{13b}$$

if $c_{2e}=8c_{2i}$. Namely, the extracule radius R_{2e} is approximately half the intracule radius R_{2i} for this special choice of the contour values c_{2e} and c_{2i}. Furthermore, Eq. (13b) suggests that the radii R_{2e} and R_{2i} have an approximate proportionality relation for other combinations of c_{2e} and c_{2i}, and hence the extracule radius R_{2e} also has a correlation with the relative atomic size R_1. Using the Hartree–Fock extracule densities $d(R)$ reported in Refs. 10, 11, and 13, we have numerically verified that the above anticipation is true. Figure 3 exemplifies the correlation between R_{2e} and R_{2i} for $c_{2e}=8c_{2i}=8\times10^{-7}$. For this case, we obtain regression lines,

$$R_{2e}\cong0.5042R_{2i}-0.0719, \tag{14a}$$

$$R_{2e}\cong1.2722R_1-1.5244, \tag{14b}$$

with correlation coefficients 0.9999 and 0.9932, respectively. Equations (14a) and (14b) are consistent with Eq. (12a). Comparison of the R_{2e} values (from $c_{2e}=8\times10^{-7}$) with the univalent radii[21] gives a scaling relation

$$\bar{R}_{2e}=0.6651R_{2e}-18.5773 \quad \text{(in pm)} \tag{14c}$$

for the relative sizes of atoms. The scaled extracule radii $\bar{R}_{2e}$ are essentially the same as $\bar{R}_{2i}$ for all the 102 atoms; the average difference is 2.2 pm with the maximum 4.7 pm at the Fr atom. Thus the differences between $\bar{R}_{2e}$ and $\bar{R}_1$ are analogous to those between $\bar{R}_{2i}$ and $\bar{R}_1$ discussed before. Examples of $\bar{R}_{2e}$ are given in Table I for the fourth period atoms.

IV. SUMMARY

When a density contour approach has been applied, the distributions of the electron-pair intracule and extracule densities have been shown to reflect the relative sizes of atoms. For a particular choice of the contour values, we have $R_{2e}\cong R_{2i}/2$ for the extracule R_{2e} and intracule R_{2i} radii. If appropriate scaling relations are introduced, all the three scaled radii, $\bar{R}_1$ from the single-electron density, $\bar{R}_{2i}$ from the intracule density, and $\bar{R}_{2e}$ from the extracule density, have been found to predict essentially the same sizes for the 102 atoms from He ($Z=2$) to Lr ($Z=103$). A numerical table of the radii is available upon request.

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[1] A. J. Coleman, Int. J. Quantum Chem., Symp. **1**, 457 (1967).
[2] A. J. Thakkar, in *Density Matrices and Density Functionals*, edited by R. M. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), pp. 553–581.
[3] R. J. Boyd and J. M. Ugalde, in *Computational Chemistry*, Part A, edited by S. Fraga (Elsevier, Amsterdam, 1992), pp. 273–299.
[4] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[5] P. E. Regier and A. J. Thakkar, J. Phys. B **17**, 3391 (1984).
[6] T. Koga and H. Matsuyama, J. Chem. Phys. **107**, 8510 (1997).
[7] H. Matsuyama, T. Koga, E. Romera, and J. S. Dehesa, Phys. Rev. A **57**, 1759 (1998).
[8] A. Sarsa, F. J. Galvez, and E. Buendia, J. Chem. Phys. **109**, 7075 (1998).
[9] A. J. Thakkar and N. J. Moore, Int. J. Quantum Chem. **S15**, 393 (1981).
[10] T. Koga and H. Matsuyama, J. Chem. Phys. **108**, 3424 (1998).
[11] T. Koga, H. Matsuyama, E. Romera, and J. S. Dehesa, Phys. Rev. A **57**, 4212 (1998).
[12] F. J. Galvez, E. Buendia, and A. Sarsa, J. Chem. Phys. **111**, 3319 (1999).
[13] T. Koga and H. Matsuyama, J. Chem. Phys. **111**, 9191 (1999).
[14] T. Koga, J. Mol. Struct.: THEOCHEM (in press).
[15] T. Koga and H. Matsuyama, J. Chem. Phys. **107**, 10062 (1997); J. Phys. B **30**, 5631 (1997).
[16] J. M. Mercero, J. E. Fowler, C. Sarasola, and J. M. Ugalde, Phys. Rev. A **59**, 4255 (1999).
[17] T. Koga and H. Matsuyama, J. Phys. B **31**, 3765 (1998).
[18] T. Koga and H. Matsuyama, J. Mol. Struct.: THEOCHEM **461–462**, 261 (1999); Theor. Chem. Acc. **99**, 320 (1998); *ibid.* **102**, 39 (1999); J. Phys. B **31**, 5105 (1998).
[19] R. J. Boyd, J. Phys. B **10**, 2283 (1977).
[20] *CRC Handbook of Chemistry and Physics*, 75th ed., edited by D. R. Lide (CRC Press, Boca Raton, 1994).
[21] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, 1960).

[22] R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3341 (1967).
[23] P. E. Cade, R. F. W. Bader, W. H. Henneker, and I. Keaveny, J. Chem. Phys. **50**, 5313 (1969).
[24] E. Clementi, IBM J. Res. Dev. **9**, 2 (1965).
[25] C. Roetti and E. Clementi, J. Chem. Phys. **60**, 3342 (1974).
[26] C. F. Bunge, J. A. Barrientos, A. V. Bunge, and J. A. Cogordan, Phys. Rev. A **46**, 3691 (1992).
[27] T. Koga, H. Tatewaki, and A. J. Thakkar, Phys. Rev. A **47**, 4510 (1993); T. Koga, S. Watanabe, K. Kanayama, R. Yasuda, and A. J. Thakkar, J. Chem. Phys. **103**, 3000 (1995).
[28] T. Koga, Theor. Chim. Acta **95**, 113 (1997).
[29] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra.* NSRDS-NBS 34 (Natl. Bur. Stand. U.S., Washington, DC, 1970).
[30] H. L. Anderson, *A Physicist's Desk Reference* (AIP Press, New York, 1989), p.94.