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Radial dependence of exterior electron distributions of molecular orbitals*

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A molecular surface is introduced to divide interior electron densities from exterior electron densities (EED). The radial distribution of EED (RADEED) is defined for each molecular orbital as a function of the distance from the molecular surface. Logarithmic plots of RADEED for NH_3 using various basis sets in *ab initio* MO calculations revealed some important features: (i) the Hartree-Fock limit for the orbital function tail may be suggested and thus qualities of basis sets can be discussed, and (ii) the slope of the curve shows the decay rate of the orbital which can be compared with the curve derived from the theoretical behavior of the long-range asymptotic form involving either the lowest ionization potential or the orbital energy of the highest occupied orbital.

Key words: Wavefunction tail — *Ab initio* wavefunction — Basis set — NH_3

Introduction

In recent decades, experimental developments have aroused great interest about wavefunction tails which often play essential roles in various intermolecular interaction processes including energy transfer, charge transfer and molecular collisions [1-4]. Their importance is also of note for molecular systems in diffuse electronic states, such as a Rydberg state [5] or a negative ionic state [6]. Since computed results for these problems depend crucially on the accuracy of wavefunction tails, one cannot avoid inspecting the quality of wavefunctions and basis functions used in the calculations.

It is well known that the cusp ratio, $(\partial\phi/\partial r)/\phi$[7], which is simply related to the atomic number, is a general index to test the accuracy of a computed atomic

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[*] Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

wavefunction for the gradient at the atomic nucleus. Even in molecules, the cusp ratio, if it is obtained by taking a spherical average at the position of each atom, is related to the relevant atomic number [8]. As for the asymptotic long-range behavior an exponential dependence on a radial parameter r, $\sim\exp(-\alpha r)$, where the decay constant α is related to the lowest ionization potential [9-18] or the orbital energy of the highest occupied orbital [19] has been suggested for wavefunctions [9-11], charge densities [12-18], natural orbitals [11-14] and Hartree-Fock orbitals [19]. Such a theoretical constraint on the long-range behavior has been used to test the electron density of the ground state of helium [20]. The long-range behavior of natural orbitals for helium atom has been studied in this way [21, 22]. In order to make a numerical analysis of the long-range behavior of molecular wavefunctions or molecular orbitals, however, there are some inherent problems arising from lack of spherical symmetry:

(i) how to define a unique radial distance from a molecule, and

(ii) how to make a directional average of wavefunction tails for anisotropic systems.

Since in the LCAO (linear combination of atomic orbitals) approximation molecular orbitals are fundamentally made up of a superposition of constituent atmoic orbitals, tails of MOs (molecular orbitals) can also be considered as a superposition of tails of atomic orbitals. This implies that distances from atomic centers are most important for the analysis of orbital function tails. In a polyatomic molecules, however, these distances are different in general for individual atoms in the molecule. This complexity may be removed by adopting the shortest of the distances. This nearest-atom approximation is reasonable provided that the system contains atoms of the same size. In order to consider different-sized constituent atoms, it is almost necessary to introduce a boundary surface to a molecule, that is a molecular surface, which reflects the sizes of constituent atoms. This is easily done by introducing a boundary surface or a radius for each atom which is then superposed into a molecular boundary surface.

The molecular surface so obtained divides the whole space Ω into two parts, the interior region Ω_i and the exterior region Ω_e: $\Omega = \Omega_i + \Omega_e$. On this basis, integrated electron densities for each orbital function ϕ are divided into two parts, the interior electron density (IED) and the exterior electron density (EED),

$$(\mathrm{IED}) = \int_{\Omega_i} |\phi|^2 \, d\tau \quad \text{and} \quad (\mathrm{EED}) = \int_{\Omega_e} |\phi|^2 \, d\tau.$$

From the normalization condition,

$$(\mathrm{IED}) + (\mathrm{EED}) = 1.$$

This IED/EED concept has been used to study (i) the basis-set dependence of *ab initio* MO function tails [23] and (ii) the role of wavefunction tails in an atom-molecule collision reaction process [24]. In this article a method to evaluate radial distributions of tails of molecular orbitals is presented. *Ab initio* MO function tails are then analyzed for NH_3.

1. Radial dependence of exterior electron distributions

1.1. Radial distribution function of EED

Once a molecular surface dividing the interior region from the exterior region is introduced, then any point in the exterior region has a unique shortest distance R from the molecular surface. With this parameter R, one may integrate the orbital electron density $|\phi|^2$ for a region between R and $R+dR$:

$$D(R)\,dR = \int_{R}^{R+dR} |\phi|^2\,d\tau.$$

Here, $D(R)$ is the radial distribution function of the exterior electron density (EED):

$$(\mathrm{EED}) = \int_{0}^{\infty} D(R)\,dR.$$

2.2. Molecular surface

One of the simplest models of the molecular surface is the van der Waals surface (vdW surface) which is made up of atoms with standard radii, so-called van der Waals radii. Although this model is an approximation of the molecular repulsive surface, *ab initio* MO calculations of exterior electron densities (EED) for occupied MOs using this vdW surface model gave EED values that are related to experimental Penning ionization cross sections for some simple molecules [4] and hydrocarbon molecules [24]. This means that the vdW surface behaves as an effective boundary for dividing exterior reactive electrons from interior inactive electrons. In view of these findings, the vdW surface model was also used in the present study.

2. Calculations

One of the most suitable systems for the present study is a molecule having lone-pair electrons. A typical example is the NH_3 molecule, for which exterior electron distributions were found to be very sensitive to the choice of basis functions for an MO calculation [23]. In the present study, radial distributions of exterior electron densities were calculated for orbitals of NH_3.

The radial distribution function of EED, $D(R)$, was calculated by counting electron densities at cubic lattice points involved in a sub-region between R and $R+\Delta$. The thickness of the subregion Δ was chosen to be 0.1 Å. The exterior region up to 2 Å from the vdW surface was divided into subregions with thickness Δ. The far outer region was found to be less important, since in EED calculations contributions from the outer region ($R > 2$ Å) were negligibly small [23]. The parameter of the cubic lattice was chosen to be between 0.05 Å and 0.30 Å according to the necessity for obtaining reasonable accuracy in each subregion. Van der Waals radii used for the estimation of the molecular surface were as follows: $r_H = 1.20$ Å and $r_N = 1.50$ Å.

Table 1. Basis sets and exponents for the most diffuse GTOs

Basis set	Nitrogen			Hydrogen	
	s	*p*	*d*	*s*	*p*
STO-6G	0.1846836	0.1846836	—	0.1001124	—
4-31G	0.2259642	0.2259642	—	0.1612778	—
6-311G	0.2008780	0.2008780	—	0.1027410	—
6-311G*	0.2008780	0.2008780	0.913	0.1027410	—
6-311G**	0.2008780	0.2008780	0.913	0.1027410	0.75
6-311G**$d'p'$	0.2008780	0.2008780	0.2008780	0.1027410	0.1027410
HDD2G	0.0066	0.0051	—	0.1027410	—
4-31+G	0.0639	0.0639	—	0.1612778	—
6-311+G	0.0639	0.0639	—	0.1027410	—
4-31'G	0.1129821	0.2259642	—	0.1612778	—
6-311'G	0.0836992	0.2008780	—	0.1027410	—
56CGTO	0.07413	0.07943	0.42	0.0525442	0.20065

Ab initio MO calculations were performed at the computer center of the University of Tokyo with a library program GSCF2 [25]. The basis sets employed in the present study are listed in Table 1 together with exponents for the most diffuse GTOs (Gaussian type orbital). Further details of the basis sets and EED calculations were described in a previous paper [23].

3. Results and discussion

3.1. General remarks on the EED values and orbital characteristics

Table 2 shows EED values for *ab initio* molecular orbitals of NH_3 calculated with various basis sets. For the STO-6G set the EED value of the $3a_1$ orbital is

Table 2. Basis set dependence of exterior electron densities (EED) for NH_3

Basis set	Energy/a.u.	EED				
		$3a_1$	1e	$2a_1$	$1a_1$	*d*
STO-6G	−55.9882	0.0134	0.0233	0.0183	0.0001	0.0305
4-31'G	−56.9882	0.0656	0.0305	0.0318	0.0008	0.0106
4-31G	−56.1025	0.0504	0.0308	0.0104	0.0010	0.0116
4-31+G	−56.1101	0.0776	0.0312	0.0113	0.0009	0.0021
6-311'G	−56.1517	0.0769	0.0306	0.0176	0.0000	0.0033
6-311G	−56.1777	0.0602	0.0304	0.0126	0.0000	0.0067
HDD2G	−56.1790	0.0736	0.0294	0.0121	0.0000	0.0006
6-311+G	−56.1813	0.0786	0.0305	0.0125	0.0000	0.0025
6-311G**$d'p'$	−56.1893	0.0724	0.0323	0.0119	0.0000	0.0011
6-311G*	−56.2012	0.0593	0.0319	0.0130	0.0000	0.0072
6-311G**	−56.2102	0.0562	0.0319	0.0128	0.0000	0.0087
56CGTO	−56.2219	0.0736	0.0306	0.0122	0.0000	0.0000

smaller than those of the 1e and $2a_1$ orbitals, whereas for other basis sets there is a tendency for EED values to increase from the inner $1a_1$ orbital to the outermost $3a_1$ orbital. Except for the STO-6G set the following comments can be made. The $1a_1$ orbital is the inner shell 1s orbital of N and it gives a negligibly small EED value. The $2a_1$ orbital is the 2s inner valence orbital of N and it shows an EED value between 0.010 and 0.013 except for a few cases. The 1e orbital is the valence NH bonding orbital and it has an EED value of ca. 0.030. The $3a_1$ orbital is the valence nonbonding orbital corresponding to the lone-pair in the VB (valence bond) scheme. EED values for this orbital are in a range from 0.05 to 0.08. EED values obtained for the STO-6G are quite different from these.

3.2. Basis set dependence of EED

Among the basis sets we used, the 56CGTO set given by Rauk et al [26] yielded the best SCF energy. One may take this near Hartree–Fock case as a benchmark in the present study. An average relative discrepancy (d) of EED values can be defined for each basis set by the following equation:

$$d=\left[\sum_{i=1}^{4}\{(\mathrm{EED})_i-(\mathrm{EED})_i^{56\mathrm{CGTO}}\}^2/4\right]^{1/2}.$$

The last column in Table 2 shows this quantity d.

Important remarks are summarized as follows:

(i) The minimal set (STO-6G) shows the largest discrepancy. This is apparently due to lack of flexibility for valence electrons.

(ii) Results become much better on going from the minimal (STO-6G), to the double-valenced (4-31G) and then to the triple-valenced set (6-311G). This is quite reasonable in view of the increase of flexibility of basis functions in the exterior region.

(iii) Introduction of a single set of polarization functions (6-311G*, 6-311G**) with typical exponents gives rather worse results for EED. Although this seems unusual from the view of their energies, it is not surprising because electron distributions in the interior region are adjusted variationally at the cost of deformation of wavefunction tails which are less effective in the energy minimization. When the exponents for the polarization functions (6-311G**) are changed from usual values ($d_N=0.913$, $p_H=0.75$) to more diffuse ones ($d'_N=0.200878$, $p'_H=0.102741$; 6-311G** $d'p'$ in Tables 1 and 2), EED values become considerably better agreeing with those for the 56CGTO.

(iv) Diffuse *sp*-function agumented basis sets (4-31+G, 6-311+*G*) [6] yield results superior to the original versions (4-31G, 6-311G). This gives us the important result that a correct description of wavefunction tails requires inclusion of diffuse *sp*-functions.

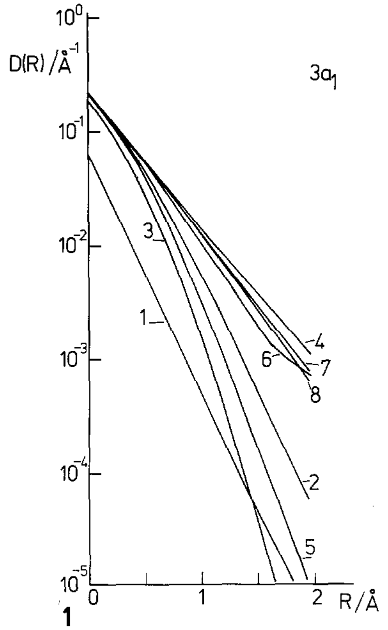
(v) The 4-31′G and 6-311′G sets are produced by a simple replacement of the most diffuse *s*-type function with a more diffuse one [23]. These sets showed much better EED values, especially for the $3a_1$ orbital, compared with the orginal versions (4-31G and 6-311G). EED values for the $2a_1$ orbital were, however, found to be rather too large.

(vi) The HDD2G set yields an almost perfect coincidence with the 56CGTO case. The HDD2G is a special basis set (11s7p)/[5s4p] for nitrogen proposed for describing Rydberg states [5], and therefore it has a great flexibility in the exterior region.

3.3. Radial distributions of exterior electron densities (RADEED)

Figures 1-3 show radial distributions of exterior electron densities (RADEED) for $3a_1$, 1e and $2a_1$ orbitals of NH_3. Each curve was plotted on a logarithmic scale as a function of the radial distance (R) from the van der Waals surface.

The 1e (NH bonding) orbital shows the smallest basis set dependence, as expected from the smallest varieties of the EED values in Table 2. In Fig. 2 two types of curves start at $R=0$; one of them is the curve for the STO-6G basis set and the other involves curves for other basis sets of contracted gaussian type orbitals (CGTO) including the 56CGTO set. The curve for the STO-6G is a very straight line. This seems to be a consequence of a single set of Slater-type valence functions in the minimal set. The curve for the near Hartree-Fock case (56CGTO) also



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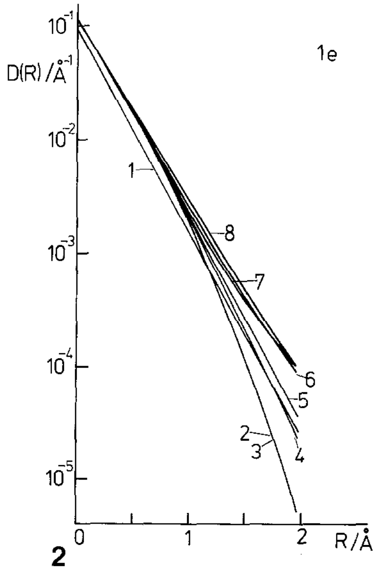

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Fig. 1. Basis set dependence of radial distributions of exterior electron densities $D(R)$ for the $3a_1$ orbital of NH_3 as functions of the distance R from the van der Waals surface. *1:* STO-6G, *2:* 4-31'G, *3:* 4-31G, *4:* 4-31+G, *5:* 6-311G, *6:* HDD2G, *7:* 6-311+G, *8:* 56CGTO

Fig. 2. Basis set dependence of radial distributions of exterior electron densities $D(R)$ for the 1e orbital of NH_3 as functions of the distance R from the van der Waals surface. *1:* STO-6G, *2:* 4-31'G, *3:* 4-31G, *4:* 4-31+G, *5:* 6-311G, *6:* HDD2G, *7:* 6-311+G, *8:* 56CGTO

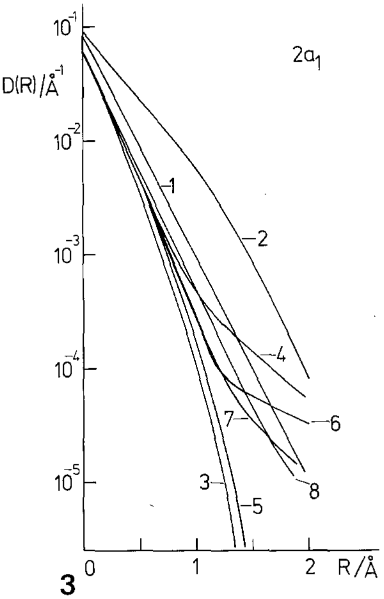
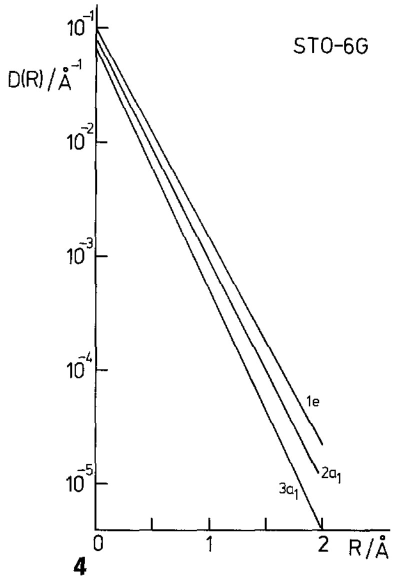


Fig. 3. Basis set dependence of radial distributions of exterior electron densities $D(R)$ for the $2a_1$ orbital of NH_3 as functions of the distance R from the van der Waals surface. *1:* STO-6G, *2:* 4-31′G, *3:* 4-31G, *4:* 4-31+G, *5:* 6-311G, *6:* HDD2G, *7:* 6-311+G, *8:* 56CGTO

exhibits approximately linear behavior , which means that the radial dependence of the oribtal function is nearly single exponential in the exterior region outside the vdW surface. Deviations from the 56CGTO curve were found to be very small for the 6-311+G and the HDD2G. This is consistent with the fact that these basis sets yield nearly the same EED values as the 56CGTO. Considerable deviations from the 56CGTO curve were found for the 4-31G and the 6-311G, especially in the outer region ($R > 1.0$ Å). This is clearly due to the absence of diffuse sp-functions in these basis sets, since the diffuse-function augmented analogues (4-31+G, 6-311+G) show considerable improvements approaching the 56CGTO case.

The $3a_1$ (N lone-pair) orbital exhibits the largest basis set dependence. The curves in Fig. 1 are grouped into two types: the STO curve, which is again in a straight line, and the CGTO curves which have a variety of branching according to the quality of the basis functions. It is of note that the CGTO curves reveal an upper bound for the $3a_1$ orbital which seems to be a straight line as in the case of 1e orbital. This suggests that in the Hartree-Fock limit the orbital function tail behaves like a hydrogenic or Slater-type atomic orbital. Deviations from the near Hartree-Fock case (56CGTO) are largely due to lack of diffuse basis functions; typical examples are 4-31G and the 6-311G.

The $2a_1$(N2s) orbital gives rather complex behavior. The STO curve again shows a straight line. However, in this case the STO curve is mostly above the CGTO curves. This is in contrast with the case for the $3a_1$ orbital for which the STO curve is far below the CGTO curves. This point will be discussed later. Among the CGTO curves for the $2a_1$ orbital, the largest downward deviation from the straight line is again found for the 4-31G set. It is interesting that upward



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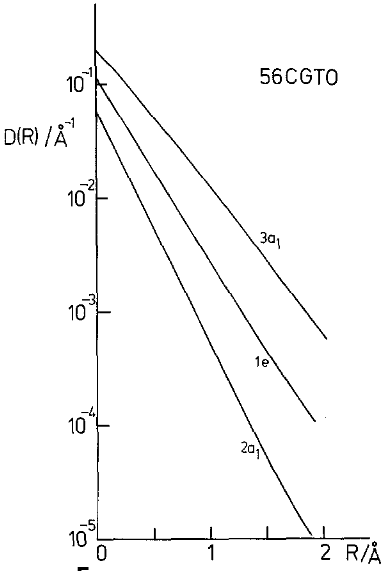

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Fig. 4. Radial distributions of exterior electron densities $D(R)$ of orbitals of NH_3 for the STO-6G basis set

Fig. 5. Radial distributions of exterior electron densities $D(R)$ of orbitals of NH_3 for the 56CGTO basis set

deviations from the straight line are found in the outer region ($R > 1.2$ Å) for diffuse-function agumented basis sets (4-31+G, 6-311+G) and the Rydberg set (HDD2G). It seems really wonderful that the curve for the near HF case (56CGTO) also yields a straight line in comparison with other CGTO curves. Overshoot of the exterior electron distribution is found for the 4-31′G basis set when the most diffuse s-type function in the 4-31G set is replaced by a more diffuse one [23], whereas for the $3a_1$ orbital the 4-31′G set yields an improved result in comparison with the original set (4-31G). In the case of the $2a_1$ orbital the replaced diffuse s function seems to cause a mixing of orbital characters between the $3a_1$ and the $2a_1$ orbitals in the tail region. This may indicate that orbital function tails of s-type characters are unstable for medium size basis sets.

The STO-6G basis set, which is a typical minimal basis set, yields straight lines in the logarithmic plots of RADEED. In Fig. 4 all three valence molecular orbitals ($3a_1$, 1e, $2a_1$) give straight lines with nearly the same slope. This simple exponential dependence is mainly due to H 1s functions which are more diffuse than the N 2p and N 2s functions. Slight differences among the curves in Fig. 4 are due to relative contributions of H 1s, $(1e) > (2a_1) > (3a_1)$. These are the reason why the MO function tails calculated with the STO-6G show an order in their "sizes" and "lengths", $(1e) > (2a_1) > (3a_1)$. Here, "sizes" of orbital function tails may be defined with EED values and "lengths" may be estimated from the slopes of the log-plots of RADEED. Needless to say, the above order found for the STO-6G is contrary to our common notion that the lone-pair ($3a_1$) orbital is extending outside more than any other orbitals.

The basis sets with contracted gaussian type orbitals (CGTO) result in a number of curves in the log-plot of RADEED for each MO; the curves start along the same line at $R = 0$ and then diverge, usually downwards, when the radial parameter R (distance from the vdW surface) increases. There seems to be an extreme linear curve for each MO which is an upper bound of the CGTO curves. The largest CGTO (56CGTO) in the present study gave an approximately linear curve as the upper bound. As can be seen in Fig. 5, curves of different MOs for the 56CGTO are far apart from each other. The $3a_1$ (lone-pair) orbital gives a linear curve far above the curves for the 1e and the $2a_1$ orbitals in good accord with our notion that a lone-pair orbital has a bigger tail than bonding orbitals. It is also reasonable that the curve for the innermost valence orbital ($2a_1$) is below that for the 1e orbital.

From the slope of a log-plot, the effective decay constant α, $\alpha = -(\partial D/\partial R)/D$, can be esimtated. When the inclination is constant, $D(R) = D(0)\ e^{-\alpha R}$. In the range 1.5–2.0 Å from the vdW surface, curves for the 56CGTO (Fig. 5) converge to become nearly parallel; estimated values of α are $3.1 \sim 3.2$ Å^{-1} for $3a_1$, $3.5 \sim 3.3$ Å^{-1} for 1e and $4.0 \sim 3.4$ Å^{-1} for $2a_1$. On average, the asymptotic value of α is about $3.2 \sim 3.4$ Å^{-1}. This can be compared with the value of the decay parameter α expected from the theoretical asymptotic form [9–18], $\alpha = 2(2I_p)^{1/2}$, where I_p is the lowest ionization potential. The experimental value of I_p for NH_3 (10.85 eV) leads to $\alpha = 3.38$ Å^{-1}. If one uses the asymptotic condition for Hartree-Fock orbitals derived by Handy et al. [19], ($\alpha = 2(-2\varepsilon)^{1/2}$ where ε is the orbital energy of the highest occupied orbital) the value of α is calculated to be 3.50 Å^{-1} from $\varepsilon = -11.64$ eV (56CGTO). Therefore, the α-value obtained from the slope of the log-plots of RADEED is shown to be consistent with the theoretical values from the asymptotic form. In view of the approximation involved in our analysis, such a coincidence of the α-values may be surprising. The present results seem to give support to the long range asymptotic condition that exponential decay constants for Hartree-Fock orbitals are common to all orbitals [19].

Based on these findings one may conclude that the upper boundary of CGTO curves such as the curve for the 56CGTO possibly indicates the Hartree-Fock limit. From this the following criteria to obtain accurate orbital function tails may be deduced.

1. When a log-plot of RADEED is far from linear, the orbital function does not have an accurate tail. If the curve declines downwards, the basis set used is deficient in diffuse functions, so MO calculations can be improved by adding some diffuse functions in the basis sets. If the curve overshoots considerably upwards, there is a possibility that, although the basis set has very diffuse functions, it lacks functions with medium exponents for describing the valence region. Overshooting often accompanies false nodes in the tail region of the coordinate space. If this is so, attempts should be made to remove the false nodes as well as overshooting in RADEED.

2. When curves in the log-plots are almost linear, the slopes of the curves should be examined. When curves for different molecular orbitals are nearly parallel on going in the outer region, the set of orbitals has a common tail of the same decay rate in agreement with the theoretical constraint. If the inclination of the curves is consistent with that expected from the lowest I_p, the soundness of the orbital function tails is confirmed. Otherwise, further trials to improve basis sets must be made.

4. Remarks on the RADEED concept

Radial dependence of electron densities might be studied in any direction if one can assume a unique central point of a molecule. This kind of analysis is suitable for systems of spherical symmetry such as atoms. However, for polyatomic molecules there are serious problems.

(i) A unique choice of a central point cannot be made except for some special systems.

(ii) A complete description of radial dependence needs to be made as a function of angle due to the anisotropy.

(iii) Even if both the above problems are solved, the radial distance from the central point does not necessarily give a good measure of the distance from the molecule. For example, in a long molecule like H—C≡C—C≡C—H, points at the same distance from the center of mass may have different distances from the molecule depending on the direction of the vector directed to each point. For example when the direction is along the long molecular axis, the point may be one of the terminal hydrogen atoms and thus be a zero distance from the molecule, whereas for a point at the same distance from the center of mass in the perpendicular direction the distance from any atom in the molecule is large.

In view of the above problems, a boundary surface reflecting geometrical size and shape of a molecule is necessary for studying molecular wavefunction tails. A boundary surface might be introduced purely from quantum mechanical calculations. This is, of course, ideal if correct wavefunctions are available. However, when one uses approximate wavefunctions, a boundary surface obtained using them is also approximate. This is therefore not a convenient way to study the quality of wavefunction tails for various basis sets, since the definition of the tail region depends upon the accuracy of each wavefunction. In view of these problems, the vdW surface was used in the present study. This choice of the boundary surface has the further advantage of being related to experiments [4, 23, 24], since the vdW surface is an approximation to the repulsive molecular surface of a classical collision.

The radial distribution function defined in the present study provides a measure of molecular orbital function tails. It reveals their asymptotic behavior. A logarithmic plot of RADEED exhibits some important features of (i) basis set qualities and (ii) orbital tail characteristics.

(i) From a number of curves corresponding to a variety of CGTO basis sets the Hartree-Fock limit of the orbital function tail is suggested and on this basis qualities of basis sets can be examined.

(ii) The slope of the curve in the log-plot shows the decay rate of the orbital function tail, and it may be compared with the theoretical constraint related to the lowest I_p or the orbital energy of the highest occupied MO.

Finally one may comment on a connection of the RADEED with experiments. Penning ionization cross sections depend on the relative velocity of a projectile metastable atom (A^*) and target sample molecules (M) [27]. When the interaction potential between A^* and M is repulsive, increasing the velocity of A^* results in a shorter turning point in the potential curve which causes an effective shrinkage of the molecular surface. Since the EED model for Penning ionization [4, 24] shows the Penning ionization cross section to be proportional to the EED value, velocity-dependence experiments will provide information about orbital function tails as well as the radial dependence of EED.

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