Chemical bonding mechanisms of n-butane probed by the core orbitals of conformational isomers in r-space and k-space

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Chemical bonding mechanisms of *n*-butane probed by the core orbitals of conformational isomers in **r**-space and **k**-space

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Abstract

Core shells of molecules are largely ignored in quantum mechanical calculations of organic compounds. A novel means of studying chemical bonding mechanisms using core molecular orbitals (MOs) of *n*-butane conformational isomers is presented in **r**-space and **k**-space. It is demonstrated that the central MOs are more sensitive to energetic properties in real space. In contrast, the terminal MO pair is more sensitive in reciprocal space, reflecting the fact that the equivalent core MOs caused by orbital energy degeneracy in **r**-space can be differentiated in **k**-space. This work provides a unique and novel channel to study isomerization and suggests that a comprehensive understanding of the bonding mechanisms of molecules can be better achieved using information from both **r**-space and **k**-space.
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1. Introduction

As a saturated alkane, butane (C_4H_{10}) is a prototype in organic chemistry for structural isomers, which differ in the constitution and connection of the atoms, such as *n*-butane ($CH_3CH_2CH_2CH_3$) and iso-butane ($CH(CH_3)_3$). Normal butane (*n*-butane) offers an interesting case in organic chemistry for the study of conformational isomers, which differ in the positions of the atoms in space. Of particular interest and importance for *n*-butane are the conformational isomers produced by rotations around the dihedral angle formed by the four carbon atoms, i.e., the minimum and maximum structures on the torsional potential surface. Butane has been intensively studied in the past few decades both experimentally and theoretically. Previous work has been summarized by Allinger et al. [1]. Butane is also a system which puzzles chemists. It is well known that iso-butane is more chemically active than *n*-butane but has lower total electronic energy, which would usually be an indication of higher stability. As a result, the additivity rules were introduced to estimate thermo-chemical properties [2,3] in organic chemistry. In

recent years, electron momentum spectroscopy (EMS) data of butane has become available for valence shell [4–6] and has been analyzed quantum mechanically [4,7,8,16, 22]. No studies have focused on the core molecular orbitals (MOs) for the bonding mechanisms of the molecule so far.

Chemists usually concentrate on valence or the frontier MOs for chemical bonding mechanisms [9]. It is common to employ the frozen core (FC) approximation in organic chemistry calculations, because most basis sets do not exhibit sufficient flexibility to accurately describe the correlation of core electrons. Care needs to be taken with this approximation for molecules with strained or unusual bonding mechanisms, in particular for molecules which cannot be displayed by simple Lewis structures [10]. In such cases, the distortion or polarization of core MOs and interaction between the core MOs and valence MOs cannot be neglected and the FC approximation breaks down, as has been demonstrated for the constitutional isomers of N_2O [11–13].

Core MOs usually have atom-localized electronic states such that the electronic structure about specific elements can be studied even in the presence of many other elements. The binding energies and orbitals of the core electrons are element specific in the core region.

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Subtle differences due to the local environment contained in orbital wavefunctions make it possible to differentiate atoms of the same element located at different inequivalent sites in a molecule, giving a simpler and more novel picture of the chemical bonding of specific elements than the largely delocalized and complex valence MOs, as can be probed by X-ray spectroscopy. Despite the usefulness of core electron related information, it is sometimes difficult to relate precisely the various binding energies with the underlying molecular structures experimentally [14], even with the application of synchrotron sources. Moreover, information from configuration space can hardly differentiate atoms of the same element located on equivalent sites of the molecule, such as the energy degenerate states of terminal core MOs in *n*-butane. In these cases, accurate quantum mechanical information in both **r**-space and **k**-space can help researchers to deduce molecular structures with a relatively high degree of accuracy and with little ambiguity.

The subtle differences in chemical bonding mechanisms due to the environmental effects of elements, such as stereo-isomerization and some energy-degenerated orbitals, are related to problems which particularly need information from **k**-space. MOs in momentum space, such as orbital momentum distributions, provide detailed structural information of the wavefunction. For example, local information at the equivalent sites (by symmetry in space) in a molecule, which is largely 'invisible' with respect to energetic properties. In this regard, combined electronic information from both **r**-space and **k**-space is needed to comprehend molecular chemical bonding. In this Letter, we use theoretical methods based on the B3LYP density functional theory (DFT) and restricted Hartree–Fock (RHF) method with the DFT triplet zeta valence polarized basis set (TZVP) [15] to study the chemical bonding mechanisms of *n*-butane, using the core MO information of four significant conformational isomers in both **r**-space and **k**-space.

2. *n*-Butane conformer orientation and symmetry

The four conformers studied are related to the most significant structures (minima and maxima) on the potential energy surface of *n*-butane generated by rotations around the dihedral angle, δ, formed by the four carbon atoms (refer to [16]). Carbon atoms in the singly bonded butane carbon chain are numbered as $C_{(3)}$–$C_{(1)}$–$C_{(2)}$–$C_{(4)}$, and the origin of the Cartesian coordinate system coincides with the mid-point of the $C_{(1)}$–$C_{(2)}$ bond. The conformations are labeled A, B, C and D for the anti ($\delta = 0°$), eclipsed ($\delta \approx 60°$), gauche ($\delta \approx 120°$) and *cis* ($\delta = 180°$) states, respectively. Conformers B and C have C_2 symmetry group, while A and D have C_{2h} and C_{2v} point groups, respectively. By convention, the principal C_2-rotational axis is the *z*-axis for all conformers.

3. Core MOs of the *n*-butane conformers in r-space

The electronic structures of the conformers were calculated at the RHF/TZVP//MP2(full)/TZVP and B3LYP/TZVP//B3LYP/TZVP levels using GAUSSIAN03 [17] for conformer energy minimization and transition state searching and GAMESS-US02 [18] for symmetry imposed single point calculations. The B3LYP/TZVP model is expected to be able to produce the same accuracy as the uGTS/BP//scaled-pVTZ/expt model [19]. It has been demonstrated that the TZVP basis set [15,20] yields competitive accuracy with the cc-pVTZ basis set for the s-, p- and d-functions [21]. We have also demonstrated previously [22] that this basis set [15] gives a reliable electron configuration for anti-butane (A, $X^1 A_g$); identical to that given by the aug-cc-pVTZ basis set [23] with the RHF method.

For carbon 1s ionization, the observed core electron binding energies (CEBEs) span more than 10 eV, from 287.2 eV in $B_3C_{12}H_{25}$ to 301.88 eV for CF_4 [24]. The energies for hydrocarbons (without significant strain) are found in the vicinity of 290 eV, since the electronegativities of carbon and hydrogen are similar [19]. Table 1 gives the core MO energies calculated in the present work and the CEBEs calculated with the 'Δ DFT' method [19] using Janak's theorem [25]. While the experimental CEBEs for *n*-butane only provided an averaged value of 290.48 eV [24] due to the nature of experiments and instrument resolution, accurate quantum mechanical calculations have been able to provide more detailed information [19]. The calculated CEBEs for *n*-butane can be used as references for comparison with the core orbital energies of the *n*-butane conformers in this work. It is shown in Table 1 that the core orbital energies consistently overestimate and underestimate the CEBEs using the RHF and DFT models, respectively, across the conformers. However, the energy trends for the central carbons and terminal carbons are the same in both the RHF/TZVP//MP2(full)/TZVP and B3LYP/TZVP//B3LYP/TZVP calculations. That is, the central carbons ($C_{(1)}$ and $C_{(2)}$ in the present work) exhibit larger core MO energies than the terminal carbons ($C_{(3)}$ and $C_{(4)}$), which are consistent with the accurately generated CEBEs of anti-butane. It should be noted that the averaged theoretical CEBE (290.84 eV) for *n*-butane [19,20], did not take the average of such energies for all possible *n*-butane conformational isomers but is simply generated from those of anti-butane (A). However, based on the core orbital energies of the conformers given in Table 1, the deviation in CEBE is expected to be small.

Table 1
Core MO energies of the four conformational isomers of *n*-butane based on RHF/TZVP//MP2(full)/TZVP and B3LYP/TZVP//B3LYP/TZVP calculations[a,b]

Sym.	A(anti-C_{2h})		B(eclipsed-C_2)		C(gauche-C_2)		D(*cis*-C_{2v})	
Orbital energy	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
MO_1	$1a_g$		$1a$		$1a$		$1a_1$	
$-\epsilon$/eV	305.13	276.52	305.15	276.52	305.16	276.53	305.17	276.53
MO_2	$1b_u$		$1b$		$1b$		$1b_2$	
$-\epsilon$/eV	305.13	276.51	305.14	276.52	305.15	276.53	305.16	276.53
MO_3	$2a_g$		$2a$		$2b$		$2b_2$	
$-\epsilon$/eV	304.98	276.33	305.00	276.35	304.97	276.97	304.97	276.32
MO_4	$2b_u$		$2b$		$2a$		$2a_1$	
$-\epsilon$/eV	304.98	276.33	305.00	276.35	304.97	276.97	304.97	276.32

[a] The accurately calculated core electron binding energies for (anti-)butane is 290.86 eV for central carbons (MO_1 and MO_2) and 290.81 eV for terminal carbons (MO_3 and MO_4) [19,20].

[b] The experimental core electron binding energy for butane is 290.48 eV [24].

Despite large energy differences between the core and inner valence MOs, there are similarities in the orbital topologies. Only orbitals with certain symmetries exist in both the core and inner valence shells. For example, only a_g or b_u symmetries in MOs of anti-butane (A) and a_1 or b_2 symmetries in the MOs of *cis*-butane (D) appear in the core and inner valence regions, whereas a_u or b_g for A and a_2 or b_1 for D exist only in the outer valence shell of the conformers. This indicates that the core and inner valence regions of *n*-butane do not contain any MOs which are anti-symmetric with respect to symmetry planes through the molecule. As a result, there are no π-bonds in these regions, though this does not imply no p-atomic orbital (AO) participating the bonding. In fact, EMS experiment [4] and our previous calculations [16] indeed show the signature of carbon 2p-AOs bonding in the inner valence shell of *n*-butane. Though energy splitting among the atom-like core MOs is small, rotation around the $C_{(1)}$–$C_{(2)}$ bond leads to large positional changes of the two terminal carbon atoms so that the MO symmetries of MO_4 of A and B flip with MO_3 of C and D as shown in Table 1.

A close examination of the calculated orbital energies shows that the core MOs can be divided into two pairs of central and terminal MOs. The central MOs represent MOs centered on $C_{(1)}$ and $C_{(2)}$ atoms, whereas the terminal MOs centered on the $C_{(3)}$ and $C_{(4)}$ atoms, as shown in Fig. 1 by the MO electron densities of anti-butane (A). When experiencing torsional forces to form conformers, it is the central carbons of the molecule which are influenced by the torsional force field significantly, whereas their position in space remains unchanged with respect to the δ angle. The terminal carbons, on the other hand, experience large changes in position and are influenced by the torsional force field indirectly through the $C_{(3)}$–$C_{(1)}$ and $C_{(2)}$–$C_{(4)}$ bonds. As a result, the core MO energy splittings are either small or zero (degenerate) within the MO pairs but relatively large between different pairs. Though small, the MO
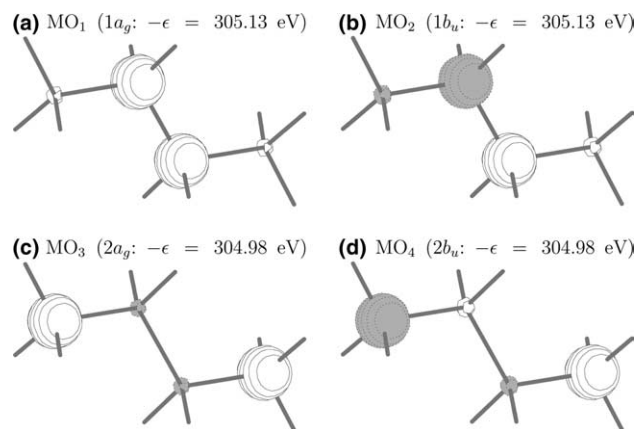

Fig. 1. Orbital electron densities of the four core MOs of anti-butane A (X^1A_g). Figures are plotted using Molden [30]. The orbital energies are based on RHF/TZVP//MP2(full)/TZVP model.

energy differences between the central and terminal MO pairs are apparently noticeable. This information implies the similar bonding mechanisms within the MO pairs but different bonding mechanisms between the pairs. Therefore, the torsional force field has a 'local' impact on the central carbon atoms, as could be expected from molecular symmetry. The terminal MO pair, concentrated on atoms $C_{(3)}$ and $C_{(4)}$, is always energy degenerate across the conformations in the **r**-space.

4. Core MOs of the *n*-butane conformers in k-space

Under the Born–Oppenheimer approximation and MO theory description for the target and ion wavefunction, the EMS cross section, σ, for randomly oriented molecules is given in the plane wave impulse approximation (PWIA) implemented in the AMOLD codes by [26]

$$\sigma = K \int d\Omega |\langle \Pi \Psi_f^{N-1} | \Psi_i^N \rangle|^2, \tag{1}$$

where the terms in this equation are given in our previous study [22]. The overlap of the initial and final electronic wavefunctions is a one-electron quantity approximated as the Dyson orbital. It may be approximated by an MO, $\psi_j(\Pi)$, using the same independent-particle model for the target and ion. Eq. (1) then reduces to,

$$\sigma = K S_j^{(f)} \int d\Omega |\psi_j(\Pi)|^2, $$

where the spectroscopic factor $S_j^{(f)}$ is the probability of a one-hole configuration j being the ion wavefunction Ψ_f^{N-1} [27].

The simulation procedure for core orbital momentum distributions of the four *n*-butane conformers is the same as mentioned previously [22], reflecting the experimental EMS conditions of *n*-butane [4]. The relationship between the azimuthal angle ϕ using a binning mode [26] through the range of $\phi = 0$–$60°$. This is equivalent to sampling different target electron momenta Π [28], where

$$\Pi = \left[(2\Pi_A \cos\theta - \Pi_0)^2 + 4\Pi_A^2 \sin^2\theta \sin^2\left(\frac{\phi}{2}\right) \right]^{1/2}. \tag{2}$$

The PWIA is a good approximation for valence orbitals as the orbital relaxation is small in the valence region [29]. However, the orbital relaxation effect can be large for core MOs so that the distorted wave impulse approximation (DWIA) may be more appropriate for core MOs. It should also be noted that the total energy of 1200 eV for the two outgoing electrons is appropriate to valence MOs of *n*-butane [4]. A much higher total energy may be needed to ionize the core MOs of *n*-butane as the ionization potential (IP) of the core MOs is significantly larger than the valence MOs of a species. For core MOs, the relativistic correction for carbon is approximately 0.05 eV [19]. However, as the present work is considering the relative ground electronic structures of the *n*-butane conformers, such a small correction incurred may be assumed to be reasonably constant when comparing different conformers [9].

The core orbital MDs of the *n*-butane conformer calculation using the RHF/TZVP//MP2(full)/TZVP and B3LYP/TZVP//B3LYP/TZVP models indicate the same trends, i.e., the C$_{1s}$-AO domination. As a result, only the B3LYP/TZVP orbital MDs are presented. Fig. 2a–d give the core orbital MDs of the individual conformers, respectively. The core orbital MDs within the same conformers are apparently different, indicating the chemical environmental differences of a specific carbon atom and individual orbital wavefunction alternation in a conformer. The core orbital MD changes across the conformers can be viewed in Fig. 2, indicating structural signatures with respect to the course of conformational isomerization. A particular transitional change can be seen between conformers B and C (Fig. 2b and c). As
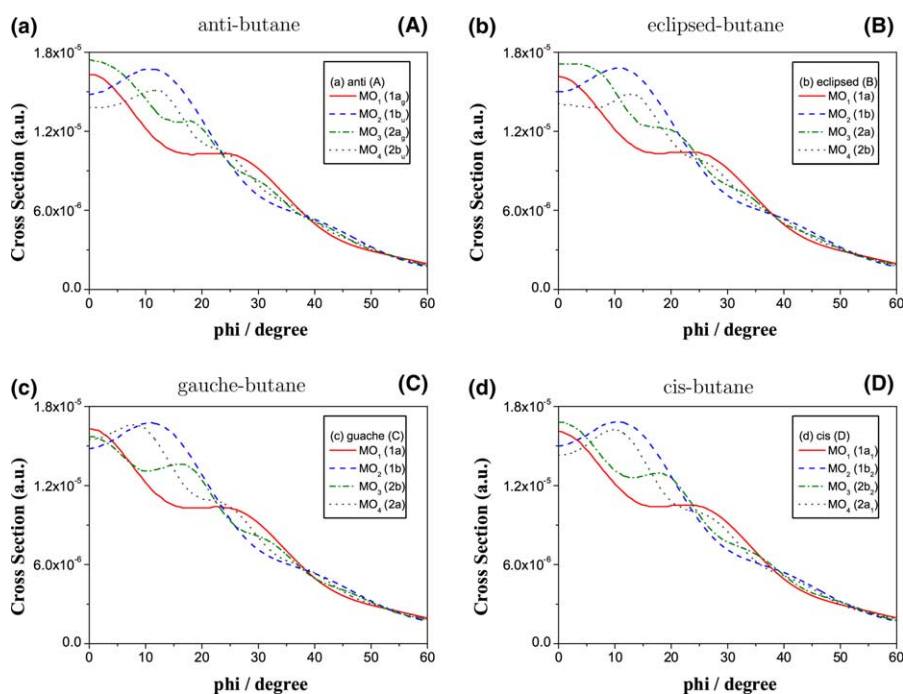

Fig. 2. Conformer based core MOs of the *n*-butane conformational isomers in **k**-space. Calculations are based on the B3LYP/TZVP//B3LYP/TZVP model.
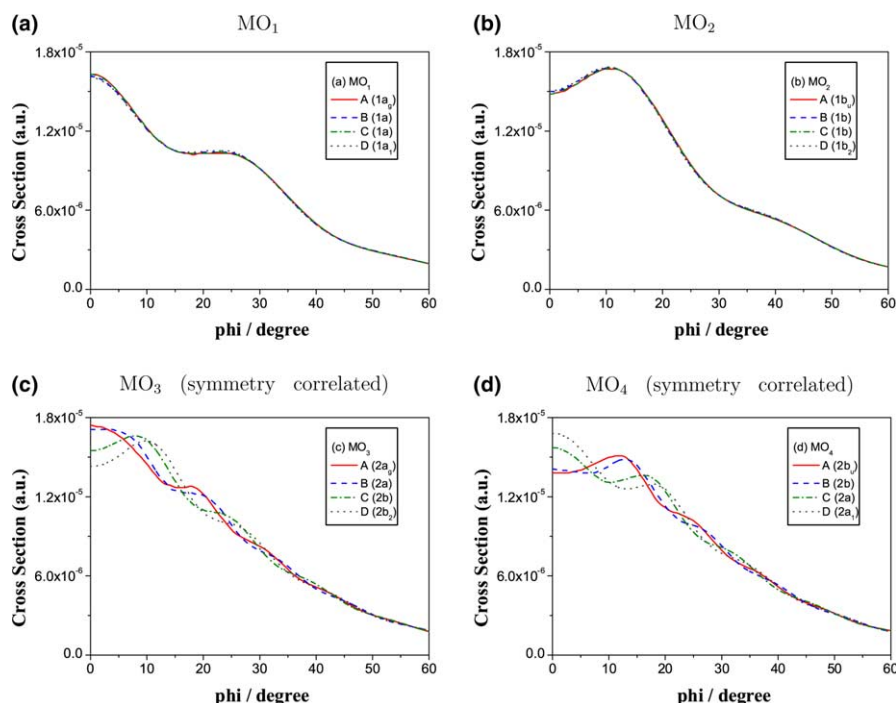
Fig. 3. Orbital based core MOs of the *n*-butane conformational isomers in **k**-space. Calculations are based on the B3LYP/TZVP//B3LYP/TZVP model.

expected, all core orbital MDs are strongly s-like MOs, dominated by contribution from the carbon C_{1s}-AOs (as also indicated in Fig. 1). The core orbital MDs expand to a larger momentum region ($\phi > 60°$) in **k**-space than the valence MOs of the same species. In the latter, the range of ϕ is $\approx 30°$ indicating that the electron densities of the core orbitals decay faster in **r**-space, i.e., a smaller 'size' for the core MOs.

If the symmetry correlated orbital MDs are presented together for the conformers on an orbital basis, the conformational impact on the core MOs during isomerization can be probed. Fig. 3a–d give the core orbital MDs of the *n*-butane conformers in **k**-space based on the B3LYP/TZVP//B3LYP/TZVP calculations. An additional feature that can be observed in momentum space is that the individual central carbon MOs (MO_1 and MO_2) across the four conformers are almost indistinguishable, whereas the terminal MOs (MO_3 and MO_4) split in small momentum regions. This demonstrates that the wavefunction in **k**-space is more sensitive to position changes (i.e., core MOs centered on the terminal carbons) but insensitive to changes of the dihedral angle δ (i.e., those centered on the central carbons). Such findings are consistent with those of the previous section.

For the rotational isomers of *n*-butane, the central carbon atoms, $C_{(1)}$ and $C_{(2)}$, are largely affected by the torsional force field as the conformers are formed, contributing to the molecular Hamiltonian and resulting in energy differentiation from the terminal carbons. The

terminal carbon atoms can only be affected by the torsional force field indirectly through $C_{(1)}$ and $C_{(2)}$ atoms in the $C_{(1)}$–$C_{(3)}$ and $C_{(2)}$–$C_{(4)}$ bonds. Change of these $C_{(1)}$–$C_{(3)}$ and $C_{(2)}$–$C_{(4)}$ bonds about the central $C_{(1)}$–$C_{(2)}$ bond rotation will not have an apparent impact on the Hamiltonian. Consequently, the central carbon core MOs are more sensitive to energetic properties in **r**-space. The energy degenerated positions with respect to the terminal carbon atoms during conformational changes, are not 'degenerate' in momentum space. In **k**-space, however, there are virtually no changes in the positions of the central carbons when undergoing conformational isomerization, so that the torsional energy changes across the conformers in MO_1 and MO_2 are nearly 'invisible', as evidenced by the core orbital MDs in Fig. 3a and b.

5. Conclusions

The chemical bonding mechanisms of *n*-butane have been studied using the core molecular orbitals in both **r**- and **k**-space based on the RHF/TZVP//MP2(Full)/TZVP and B3LYP/TZVP//B3LYP/TZVP models. Wave functions of the conformers in **r**-space are sensitive to energetic properties, such as the core MO energies, which are due to the torsional force field, as indicated by the central carbon core MOs: MO_1 and MO_2. The terminal carbon core MOs of the conformers, whose positions do not contribute directly to the molecular

Hamiltonian but experience significant changes in atomic position and symmetry, are investigated in **k**-space as they are more sensitive to momentum. In **k**-space, these positions which produce degenerate energies do not give the same momenta and can therefore be differentiated.

A comprehensive understanding of molecular electronic structure and therefore bonding mechanisms can be achieved using information from both **r**-space and **k**-space; the combination of a chemical picture (position) and a physical picture (momentum) of the species. Some molecular properties such as energetically dominated properties are in general more sensitive in **r**-space. Other properties which are more anisotropic are in general more sensitive in **k**-space. The present work contributes to the chemical bonding mechanisms of *n*-butane based on a unique and novel technique which uses the strength of quantum mechanics in both configuration space and momentum space.

Acknowledgements

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