Face-Integrated Fukui Function: Understanding Wettability Anisotropy of Molecular Crystals from Density Functional Theory

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Supporting Information

Fukui functions of aspirin and n,n-octyl-D-gluconamide (OGA) were calculated from charge densities that were obtained with a periodic *ab initio* program, Crystal 2003.[1] Calculations were performed on a 16-node Linux PC cluster in our laboratory with both Hartree-Fock (HF) and density functional theory (DFT) methods. In HF calculations, two basis sets, 3-21G and 6-21G, were employed. In DFT calculations, the B3LYP approach was chosen with the Lee-Yang-Par correlation energy and a mixing of HF exchange energy (20%) and Becke's 3-parameter exchange energy (80%). Convergence conditions in the self-consistent calculations were set as the energy difference between adjacent iterations below 10^{-6} Hartree.

Three slab structures, (100a), (100b) and (001), were built for aspirin based on its bulk crystal structure.[2] One electron was added or removed from the slabs for calculations of ionic forms. To improve the convergence, both eigenvalue level shift and Fock matrix mixing techniques were utilized. Energy values of these slabs calculated with HF 6-21G are listed in Table S1.

Effects of basis sets and calculation methods (HF and DFT) on Fukui functions were studied on aspirin slabs. Shown in Fig. S1, face-integrated Fukui functions of the (100a) slab of aspirin as well as {100} faces of aspirin bulk appear unaffected by either basis set or calculation method. The thickness of slabs or numbers of layers shows little effect on the Fukui functions, as indicated in Fig. S2.

Structural optimization was carried out for OGA. The originally reported structure had three hydrogen atoms deleted due to suspected coordinate errors.[3] We manually added these three atoms and optimized their positions with positions of other atoms fixed. The HF method with STO-3G basis set was used. The optimized structure was used to build a slab with the thickness of one unit cell resembling the (010) face. Self-consistent calculations of neutral, anionic (1 electron added) and cationic (1 electron removed) forms of the (010) face were performed with HF 6-21G. Both eigenvalue level shift and Fock matrix mixing techniques were utilized to improve the convergence, especially for ionic species. Energy values calculated were -2097.8852, -2098.7446, and -2098.5757 Hartrees for the neutral, anionic, and cationic forms, respectively. Fukui functions were derived from the difference in charge density between the neutral and anionic (010) slabs.

In addition, to study how surface reconstruction that is due to the contact with a liquid affects Fukui functions, we further optimized the OGA slab structure with a water molecule manually added to the (010) face by HF STO-3G. During the optimization, we only allowed the relaxation of the water molecule and the hydrogen of the terminal –OH group of OGA molecules. The optimized slab model with the water removed was used to calculate electronic structures of neutral and anionic forms by HF 6-21G, and to derive Fukui functions. Energy values calculated were -2097.8516, -2098.7295, and -2098.5788 Hartrees for the neutral, anionic, and cationic forms, respectively.

Reference

(1) Doll, K.; Saunders, V. R.; Harrison, N. M. *Int. J. Quantum Chem.* **2001**, *82*, 1-13.

(2) Kim, Y.; Machida, K.; Taga, T.; Osaki, K. *Chem. Pharm. Bull.* **1985**, *33*, 2641-2647.

(3) Zabel, V.; Mullerfahrnow, A.; Hilgenfeld, R.; Saenger, W.; Pfannemuller, B.; Enkelmann, V.; Welte, W. *Chem. Phys. Lipids* **1986**, *39*, 313-327.

Table S1. Energy (Hartree) calculated with HF 6-21G of aspirin slab models.

	(100a)	(100b)	(001)
Neutral form	- 2565.1802	- 2565.0905	- 2565.1818
Anionic form	- 2565.2155	- 2565.1654	- 2565.2360
Cationic form	- 2564.9344	- 2564.8336	- 2564.9610

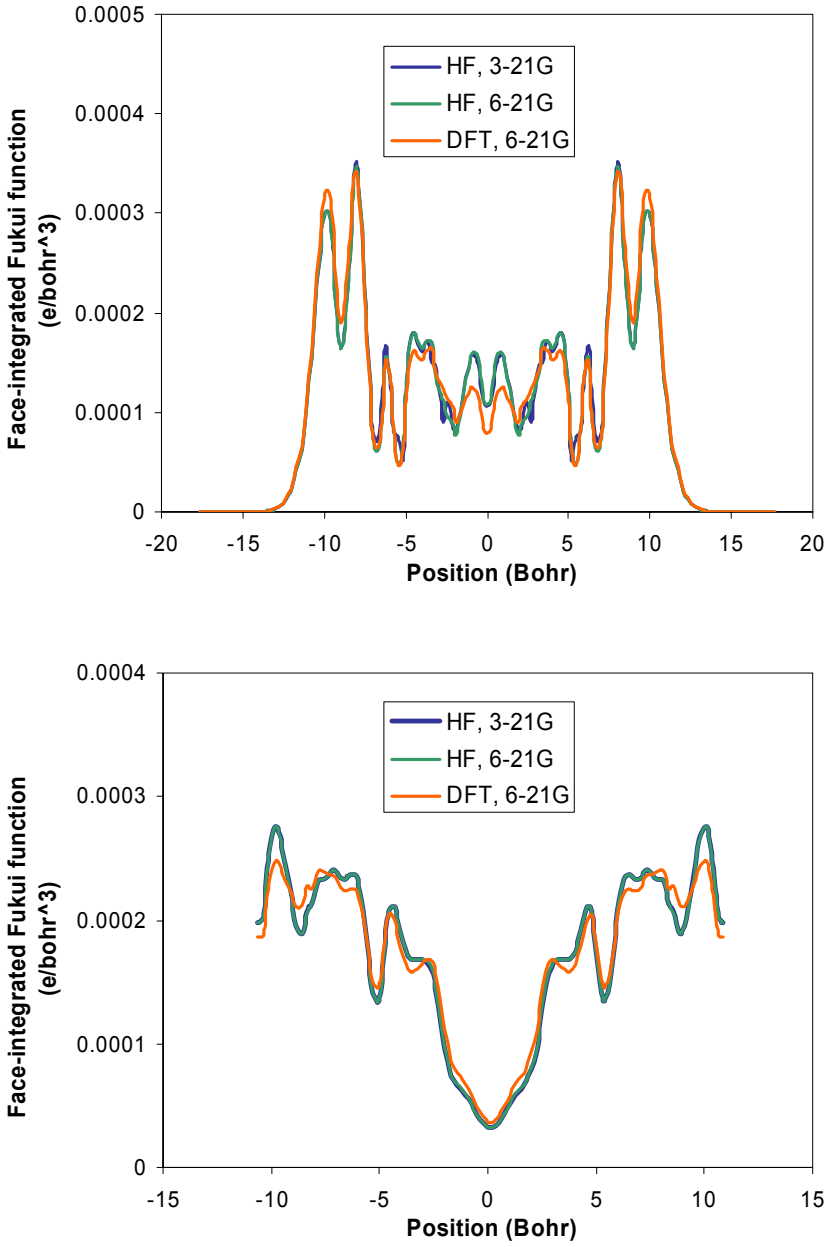

Figure S1. Effects of basis sets and methods on face-integrated Fukui functions of the (100a) slab (top) and {100} faces of aspirin bulk (bottom). The functions were calculated between charge densities of neutral and anionic forms of respective aspirin structures.

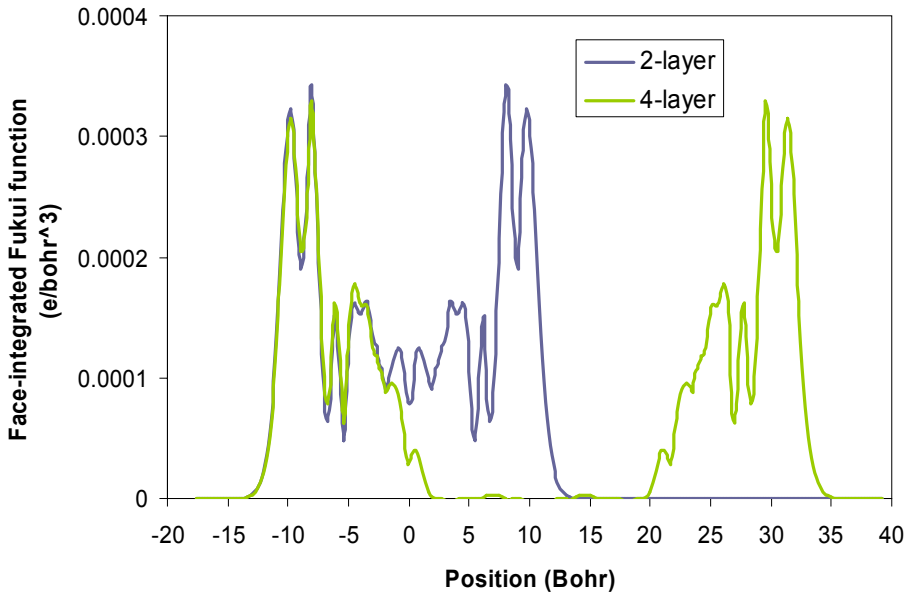

Figure S2. Effect of the model size of (100a) slabs of aspirin on face-integrated Fukui functions. The functions were calculated between charge densities of the neutral and anionic forms of respective aspirin structures with HF 3-21G.