

## 4P030

### Extended Treatment of Charge Response Kernel based on the Density Functional Theory and Charge Regulation Procedures

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We propose an extended treatment of the charge response kernel (CRK), which describes the response of partial charges on atomic sites to external electrostatic potential,  $K_{ab}$ ,

$$K_{ab} = \frac{\partial Q_a}{\partial V_b},$$

where  $Q_a$  represents the partial charge at the site a and  $V_b$  stands for the electrostatic potential at the site b, on the basis of the density functional theory (DFT) via the coupled perturbed Kohn-Sham equations. The present CRK theory incorporates charge regulation procedures in the definition of partial charges to avoid unphysical large fluctuation of the CRK on “buried” sites.[1] The CRKs of methanol, ethanol, propanol, butanol, dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) were calculated and polarizabilities for those with the CRKs were evaluated and compared with experimental results. It was shown that the new CRK model at the DFT level has greatly improved the performance of accuracy in comparison with that at the Hartree-Fock level previously proposed.[2] The present CRK model was also applied to investigate spatial nonlocality of the charge response through normal alkyl chain sequences,  $\text{CH}_3(\text{CH}_2)_n\text{OH}$  ( $n = 0 - 3$ ). Our observation indicated that the nonlocal charge

response profiles were similar behaviors among different chain lengths in the series of normal alcohols. It is considered that these results can be utilized to extending the CRK model to larger systems including alkyl chain sequences. The CRK model at the DFT level enables us to build a nonempirical strategy for polarizable models, with practical reliability and robustness.

[1] T. Ishida and A. Morita, *J. Chem. Phys.*, in press. (2006)

[2] A. Morita and S. Kato, *J. Am. Chem. Soc.* **119**, 4021 (1997)