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Environmental Theoretical Calculation for Non-periodic Systems

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Abstract

Environmental theoretical calculation aims to use computer simulation to assist in solving environmental problems. Herein, we present the guiding principles of environmental theoretical calculation for non-periodic systems. A summary is given of recent progress towards the use of environmental theoretical calculation to reveal the degradation/transformation mechanisms of contaminants in reactions.

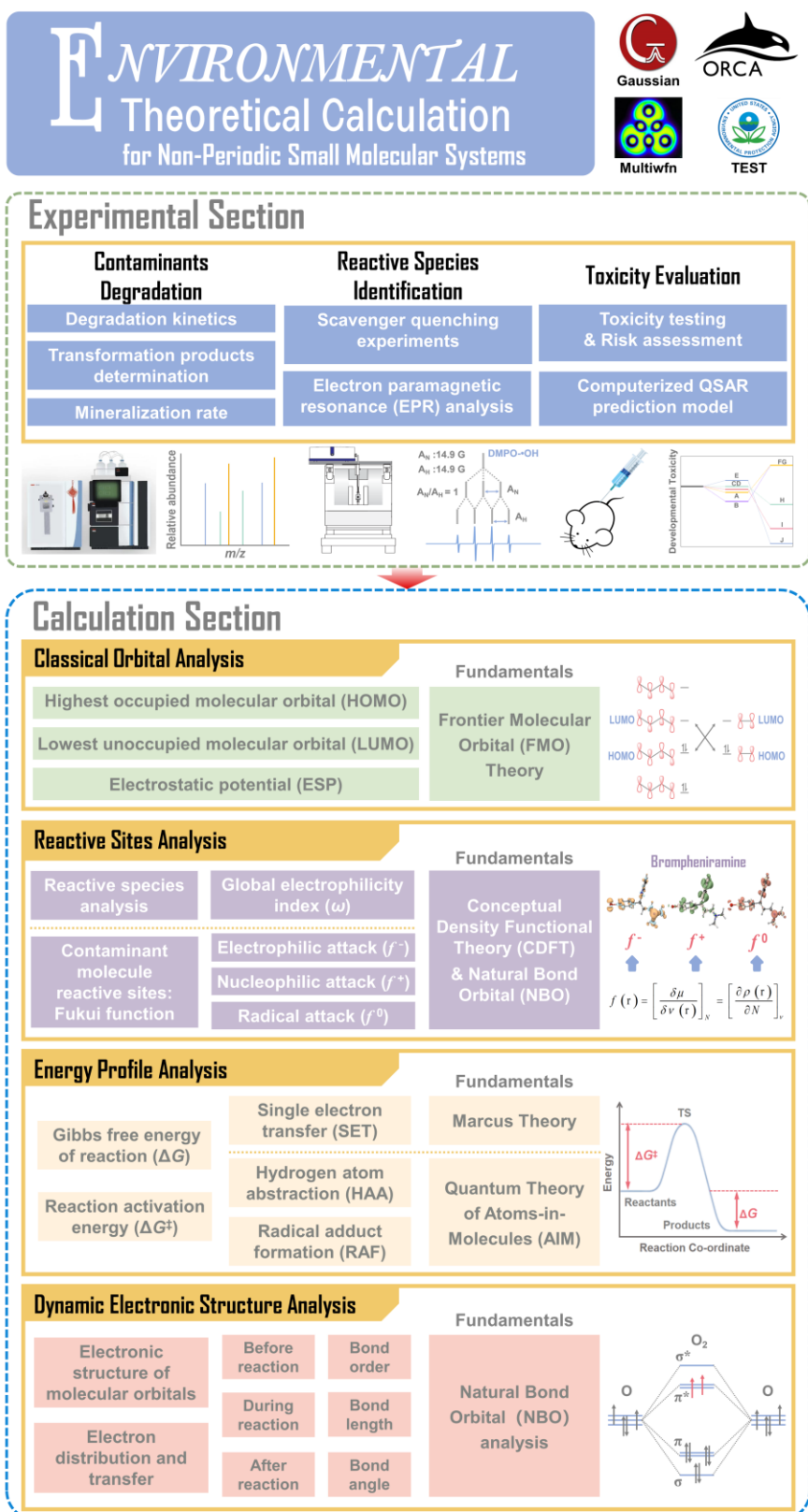
Significance of theoretical calculation in environmental research

“Beyond experiment” has been gradually accepted as a general concept in the chemistry discipline. As theoretical chemistry and computer science have advanced, it has become possible to explore the close link between macro-level observations and micro-level molecular wave functions, thus providing deep insights into chemical reaction mechanisms, the intrinsic nature of chemical behavior, and the principle of chemical phenomena [1]. Chemical reactions in an environmental system usually occur within a complicated “box” involving various oxidation/reduction reactions. More specifically, the focus has been on the transformation and degradation of a contaminant during reaction because of their close relationship to the removal and detoxification of the target contaminant. Therefore, besides conventional experimental evidence, we urgently require a theoretical calculation methodology by which to examine such reaction mechanisms in detail. Environmental theoretical calculation is a new branch of environmental chemistry defined as the application of computer simulation to assist in solving environmental problems. Theoretical calculations related to environmental research generally comprise two parts: (i) calculation of the behavior of contaminants (especially organic compounds) in order to reveal the reaction mechanism by reactive species (radicals, oxidants and reductants) through solving a finite-scale (molecule-level) problem in a non-periodic

system; and (ii) material calculations aimed at revealing physicochemical properties and the intrinsic mechanism at the material interface by solving an infinite-scale problem in a periodic system.

Environmental theoretical calculation framework for a non-periodic system

Figure 1 presents an overall framework for environmental theoretical calculation involving a non-periodic system. The reaction system for contaminant removal (especially organic contaminant degradation) is the most important non-periodic system considered in environmental research. For example, advanced oxidation processes (AOP), defined as the degradation of contaminants by highly reactive radicals, are widely applied in water treatment [2]. Invariably, in a typical environmental reaction system with contaminant degradation, a series of experiments is first conducted to obtain essential data (see Experimental Section in **Figure 1**), primarily including: i) degradation kinetics and transformation products (TPs) that determine the contaminant, ii) identification of reactive species, and iii) toxicity variation evaluation. In order for the theoretical calculation to expose the underlying mechanism, we propose the following four-step procedure (see Calculation Section in **Figure 1**): i) calculation (based on classical frontier molecular orbital (FMO) theory) of basic quantum parameters of reactive species and contaminant molecules, such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), electrostatic potential (ESP), *etc.*; ii) calculation of electrophilicity/nucleophilicity of reactive species and reactive site analysis of contaminant using Conceptual Density Functional Theory (CDFT) and Natural Bond Orbital (NBO) theory [3, 4]; iii) calculation of energy profile change using quantum theory of Atoms-in-Molecules (AIM) [5]; and iv) dynamic electronic structure analysis based on NBO theory [6].



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68 **Figure 1.** Environmental theoretical calculation framework for a non-periodic system.

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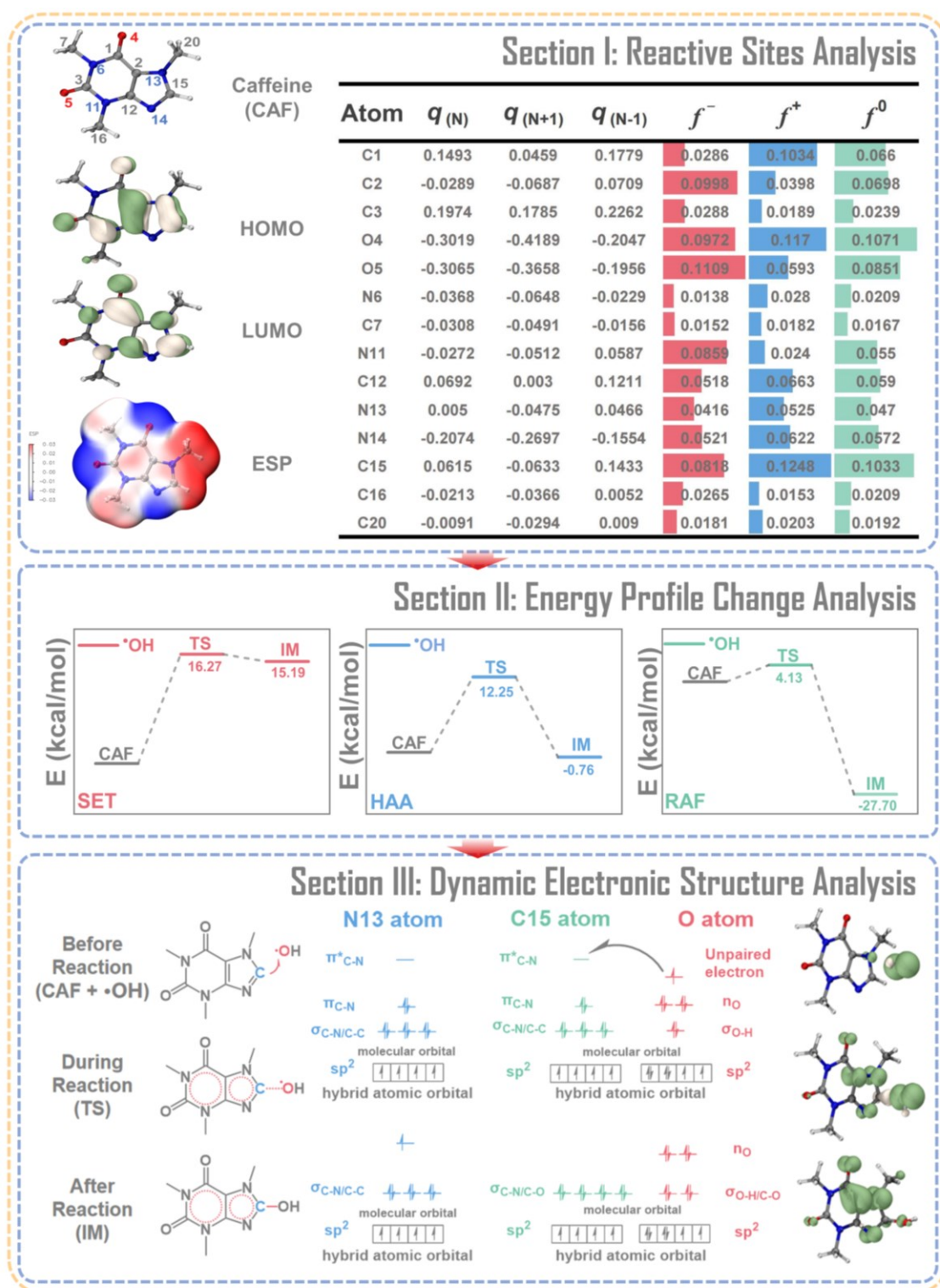


Figure 2. Theoretical calculation procedure for determining degradation of caffeine by $\cdot\text{OH}$: reactive sites and analysis (Section I), energy profile change analysis (Section II), and dynamic electronic structure analysis (Section III).

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75 For a finite system, the theoretical calculation has been performed using Gaussian
76 software [7] and ORCA [8] packages, wavefunction analysis using Multiwfn software [9], and
77 computational toxicity evaluation using the Toxicity Estimation Software Tool (TEST) based
78 on quantitative structure-activity relationship (QSAR) models [10]. **Figure 2** displays an
79 example of the environmental theoretical calculation procedure applied to the degradation of
80 caffeine by $\bullet\text{OH}$ ions.

81

82 Calculation of reactive sites of organic compounds

83 Reactive species such as radicals can be regarded as either electrophiles or nucleophiles
84 depending on their ability to attack sites of relatively high/low electron density. The global
85 electrophilicity index (ω) enables evaluation of the electrophilic or nucleophilic ability of a
86 reactive species to attack specific molecules [11], according to the electronic chemical potential
87 (μ) and chemical hardness (η) based on CDFT. The electrophilicity index leads to absolute
88 scales, which solely depend on the electronic characteristics of the electrophile and therefore
89 are independent of the nucleophilic partner. Higher ω indicates higher electrophilicity. For
90 example, in contemporary research on peracetic acid (PAA)-based AOPs [12], it has been
91 found that complicated radicals are produced, which can be divided into the following two
92 types based on global electrophilicity index: (1) a type combining two strong electrophilic
93 radicals $\text{CH}_3\text{C}(=\text{O})\text{O}\bullet$ ($\omega = 2.875$ eV) and $\bullet\text{OH}$ ($\omega = 2.811$ eV) and a weak electrophilic radical
94 $\text{CH}_3\text{C}(=\text{O})\text{OO}\bullet$ ($\omega = 2.278$ eV), with the three radicals preferentially attacking electron-rich
95 sites; and (2) moderate nucleophilic radicals $\bullet\text{CH}_3$ ($\omega = 1.209$ eV) and $\text{CH}_3\text{C}(=\text{O})\bullet$ ($\omega = 1.083$
96 eV) which preferentially attack electron-deficient sites. Thus, the global electrophilicity index

represents the selectivity of reactive species to different compounds during the reaction processes.

The environmental theoretical calculation for a given contaminant primarily investigates the reactive sites of organic compounds. In practice, the condensed Fukui function based on CDFT is widely used to predict the regioselectivity of reactive species toward a specific organic molecule [3]. The Fukui function quantifies change in electron density at a given position according to the number of electrons that have been changed. Moreover, the condensed Fukui function representing electrophilic (f^-), nucleophilic (f^+) and radical (f^0) attacks is calculated from the gain or loss of electrons (see Section I in **Figure 2**). Specifically, after geometric optimization of a molecule, its total local atomic electron population is determined by NBO analysis, following which the NBO electron populations of the corresponding cationic (-1 electron) and anionic (+1 electron) species are calculated without geometry re-optimization to obtain the condensed Fukui index. Our group has pioneered application of the Fukui function to investigate the reactive sites of organic contaminants in environmental research [13], and has established the Peking University Reactive Sites for Organic Compounds Database (PKU-REOD).

The Kohn-Sham (K-S) DFT equation (a one-electron equation) is commonly utilized within the simulation process, and its accuracy greatly depends on the selection of the exchange-correlation functional [14]. B3LYP, which is one of the most widely applied hybrid generalized-gradient approximation (GGA) functionals, performs extremely well in its description of weak interactions among molecules. In addition, as a meta-hybrid GGA functional, M06-2X is also popularly applied due to its moderate Hartree-Fock (HF) exchange (54%) and accurate description of weak interaction and dispersion effects. Meanwhile, a Gaussian-type function is selected as a primary basis function by which to solve the K-S DFT

equation, with triple-zeta Pople-style and Ahlrichs def2 basis sets preferred. To achieve a compromise between result accuracy and calculation time, the B3LYP-D3/6-311G* (6-311+G*) and M06-2X/def2-TZVP (def-TZVP) functionals are frequently utilized.

Calculation of energy profile change during reaction

The energy profile change calculation relates to reaction thermodynamics, and is used to predict the reaction equilibrium position and direction. It is difficult to measure experimentally the transition state (TS) during reaction, and so analysis of TS is a key feature of the environmental theoretical calculation method. In assessing environmental reactions for contaminants degradation, the following three typical reaction routes are commonly considered: single electron transfer (SET), hydrogen atom abstraction (HAA), and radical adduct formation (RAF) [12] (Section II in **Figure 2**). Energy profile change calculations depend on estimates of two important parameters: Gibbs free energy change (ΔG), calculated as the difference between the products and reactants of elementary processes; and activation energy (ΔG^\ddagger), calculated as the difference between TS and reactant for RAF and HAA routes. The value of ΔG^\ddagger for the SET route is usually calculated from Marcus theory [15]. For calculations based on reaction kinetics, the reaction rate constant may also be calculated from conventional transition state theory (TST).

Calculation of dynamic electronic structure during organic compound transformation reaction

To further explore the reaction mechanism and route for organic compound degradation when attacked by reactive species at the molecular orbital level, we proposed a streamlined method to interpret the dynamic electronic structure during reactive species-mediated reactions [6]. The output from this calculation includes: i) identification of reactive sites of the target organic contaminant based on the Fukui function; ii) energy profiles of radicals attacking

target organic contaminant *via* three typical routes (SET, HAA and RAF); iii) analysis of bond order, spin density and singly occupied molecular orbitals (SOMO) of the reactant (R), transition state (TS), and intermediate (IM) during reaction; and iv) details of the dynamic change of electronic structure during reaction. In a sense, dynamic electronic structure analysis offers a comprehensive calculation methodology that integrates the preceding calculations including reactive sites, energy profile change, and molecular orbitals (Section III in **Figure 2**). Our methodology can also be applied to interpret other reaction routes for contaminants degradation, such as oxygen atom transfer (OAT), proton-coupled electron transfer (PCET) and radical coupling reaction (RCR) routes. It provides deep insight into the reaction mechanism of reactive species with organic compounds, thus facilitating radical species regulation for the degradation of specific contaminants in water treatment processes.

Challenges and directions

The core challenge for environmental theoretical calculation is how to simulate complex environmental problems more accurately, thus heavily relying on advances in quantum chemistry theory and computing power. Specifically, the following research avenues need to be explored: (i) construction of more precise models that consider a variety of environmental parameters, such as solvent, speciation and charge of compound, as well as multiple coexisting substances; (ii) selection of suitable (non-random) theory and computational functions (such as polarization function, diffuse function, pseudopotential, *etc.*) for a specific system; (iii) method(s) for overcoming the very complicated geometry optimization of organic compounds (especially contaminants of large molecular weight) combined with material, so that parameters implying contaminant-material interaction (such as adsorption energy, electronic structure of the system and density of states) can be obtained more straightforwardly than at present; (iv) development of a more finely resolved quantitative analysis of reactive sites of

organic compounds, accounting for the different characteristics of reactive species, extending beyond the present rough classification into electrophilic, nucleophilic and radical attacks; (v) step-by-step analysis of the reactive route, electron transfer and bonding behavior of organic compounds during reaction, so that the key transition state and rate-limiting reaction can be identified; and (vi) use of *ab initio* molecular dynamics as a precise, unbiased method by which to observe the dynamic reaction process involved in contaminant degradation.

Concluding remarks

Environmental theoretical calculation has immense potential for solving mechanistical problems that current experiments cannot properly simulate. Herein, a systematic procedure has been proposed for profound investigation of the mechanisms underpinning environmental reaction systems. In the future, environmental theoretical calculation is expected to play a significant role in screening reactive species for the degradation of specific contaminant(s) and in regulating contaminant-orientated transformation(s) in order to satisfy environmental resource standards.

Acknowledgments

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Declaration of interests

No interests are declared.

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