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1 **Environmental Theoretical Calculation for Non-periodic Systems**

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20 **Abstract**

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

26

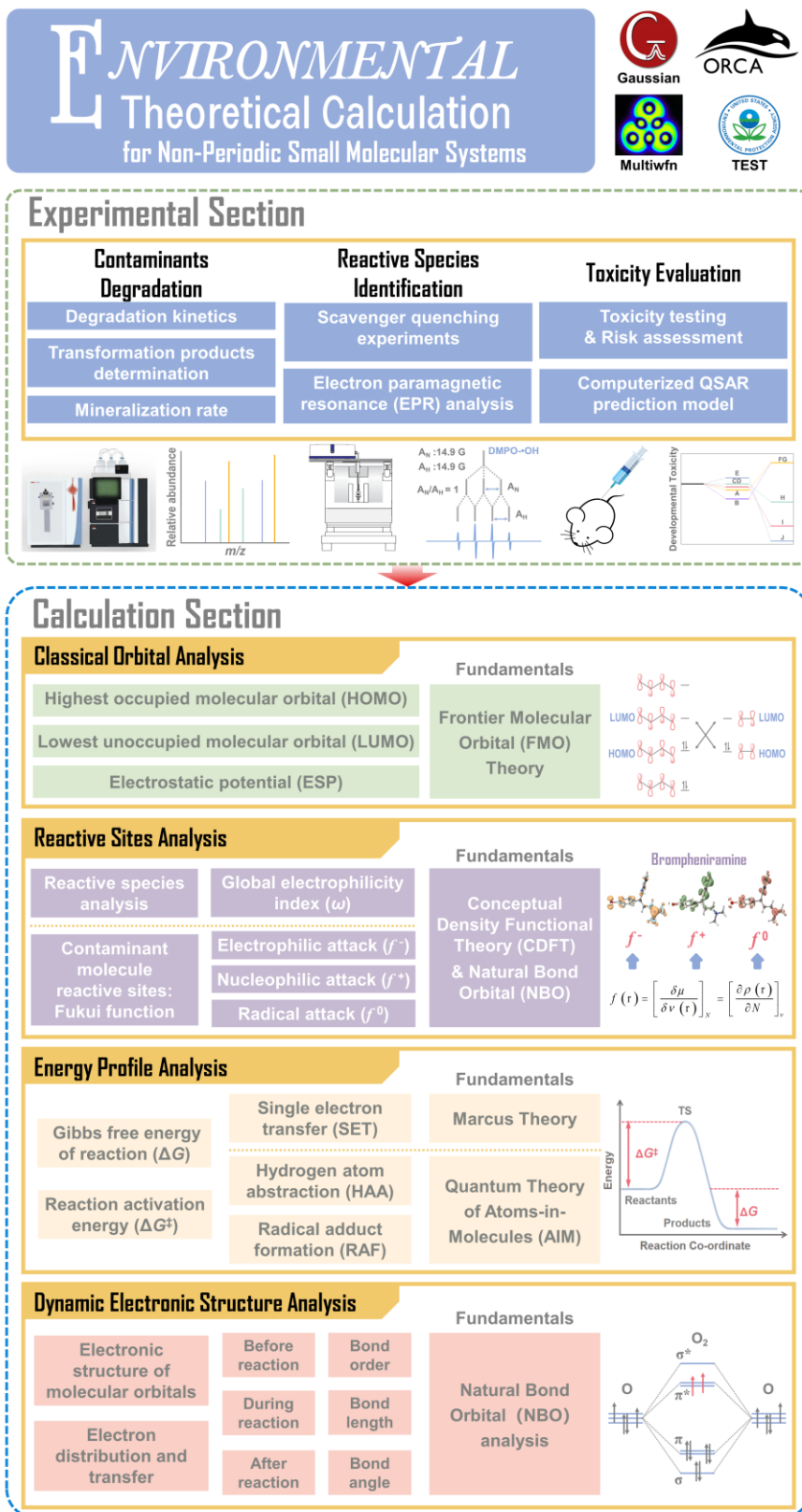
27 **Significance of theoretical calculation in environmental research**

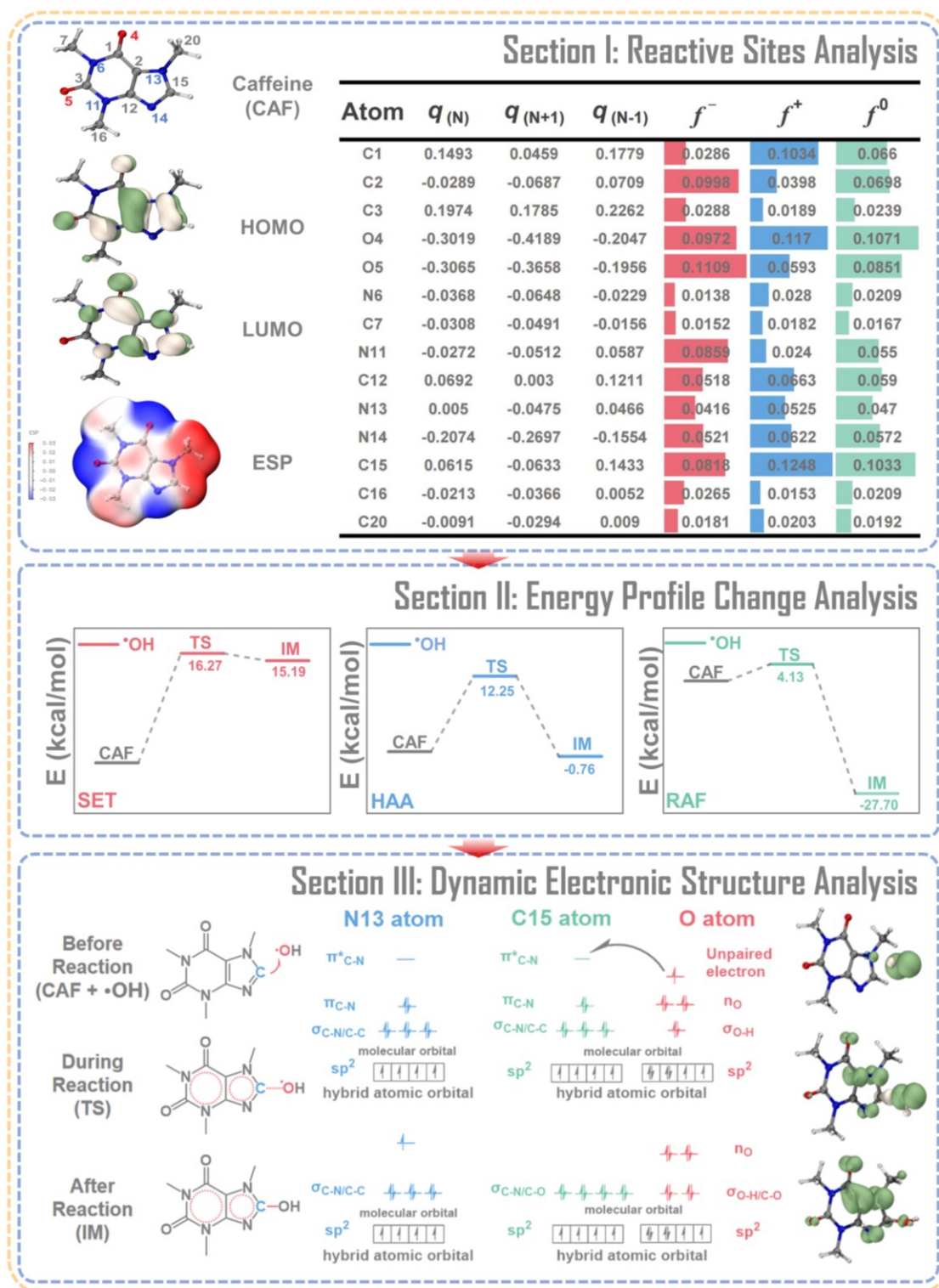
28 “Beyond experiment” has been gradually accepted as a general concept in the chemistry
29 discipline. As theoretical chemistry and computer science have advanced, it has become
30 possible to explore the close link between macro-level observations and micro-level molecular
31 wave functions, thus providing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

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

47 **Environmental theoretical calculation framework for a non-periodic system**

48 **Figure 1** presents an overall framework for environmental theoretical calculation
49 involving a non-periodic system. The reaction system for contaminant removal (especially
50 organic contaminant degradation) is the most important non-periodic system considered in
51 environmental research. For example, advanced oxidation processes (AOP), defined as the
52 degradation of contaminants by highly reactive radicals, are widely applied in water treatment
53 [2]. Invariably, in a typical environmental reaction system with contaminant degradation, a
54 series of experiments is first conducted to obtain essential data (see Experimental Section in
55 **Figure 1**), primarily including: i) degradation kinetics and transformation products (TPs) that
56 determine the contaminant, ii) identification of reactive species, and iii) toxicity variation
57 evaluation. In order for the theoretical calculation to expose the underlying mechanism, we
58 propose the following four-step procedure (see Calculation Section in **Figure 1**): i) calculation
59 (based on classical frontier molecular orbital (FMO) theory) of basic quantum parameters of
60 reactive species and contaminant molecules, such as highest occupied molecular orbital
61 (HOMO), lowest unoccupied molecular orbital (LUMO), electrostatic potential (ESP), *etc.*; ii)
62 calculation of electrophilicity/nucleophilicity of reactive species and reactive site analysis of
63 contaminant using Conceptual Density Functional Theory (CDFT) and Natural Bond Orbital
64 (NBO) theory [3, 4]; iii) calculation of energy profile change using quantum theory of Atoms-
65 in-Molecules (AIM) [5]; and iv) dynamic electronic structure analysis based on NBO theory
66 [6].





74

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

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

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

113 The Kohn-Sham (K-S) DFT equation (a one-electron equation) is commonly utilized
114 within the simulation process, and its accuracy greatly depends on the selection of the
115 exchange-correlation functional [14]. B3LYP, which is one of the most widely applied hybrid
116 generalized-gradient approximation (GGA) functionals, performs extremely well in its
117 description of weak interactions among molecules. In addition, as a meta-hybrid GGA
118 functional, M06-2X is also popularly applied due to its moderate Hartree-Fock (HF) exchange
119 (54%) and accurate description of weak interaction and dispersion effects. Meanwhile, a
120 Gaussian-type function is selected as a primary basis function by which to solve the K-S DFT

121 equation, with triple-zeta Pople-style and Ahlrichs def2 basis sets preferred. To achieve a
122 compromise between result accuracy and calculation time, the B3LYP-D3/6-311G* (6-
123 311+G*) and M06-2X/def2-TZVP (def-TZVP) functionals are frequently utilized.

124 **Calculation of energy profile change during reaction**

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

138 **Calculation of dynamic electronic structure during organic compound** 139 **transformation reaction**

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

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

156 **Challenges and directions**

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

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

175 **Concluding remarks**

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

183

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188

189 **Declaration of interests**

190 No interests are declared.

191

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