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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.

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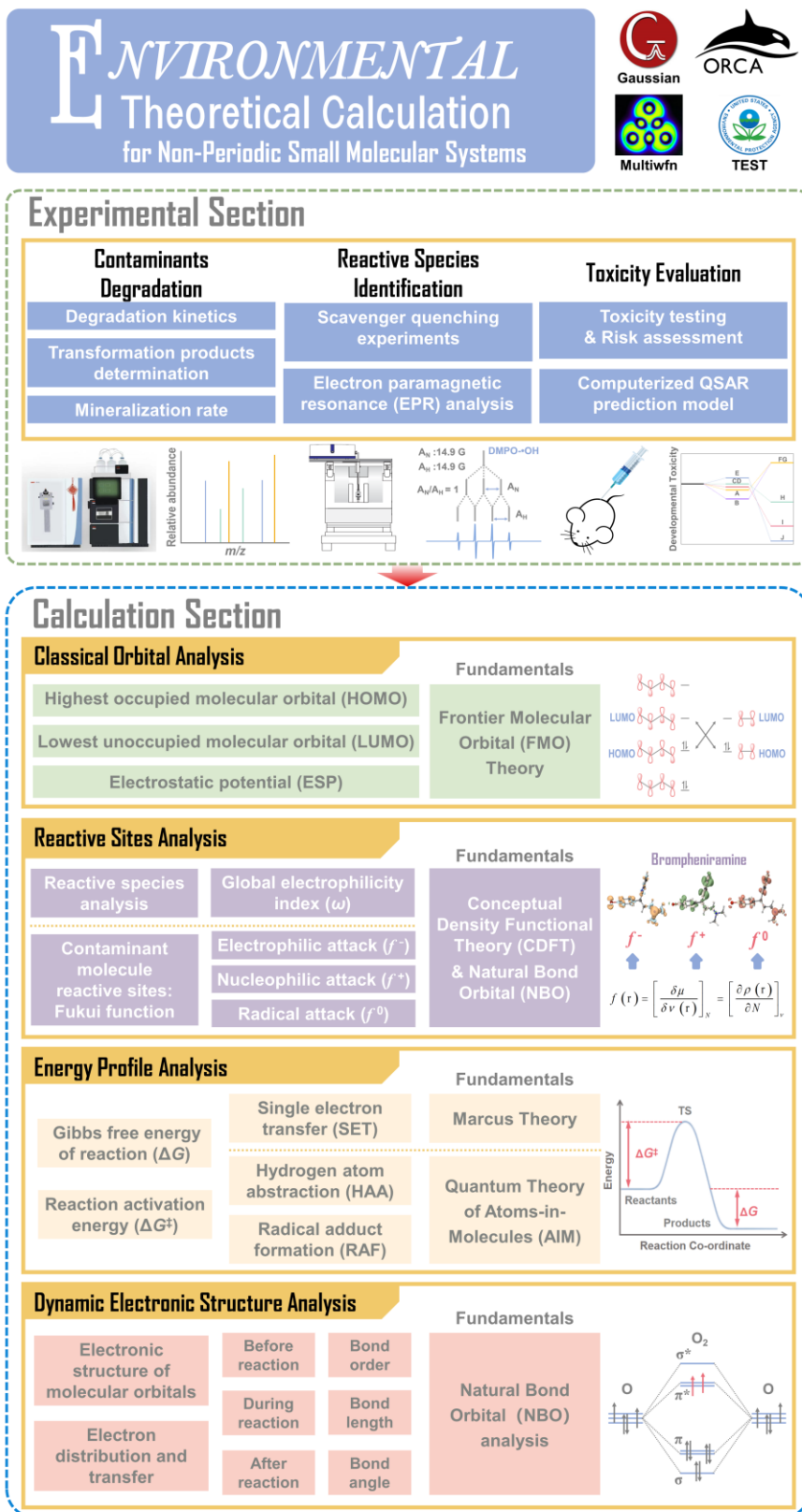
## 27 **Significance of theoretical calculation in environmental research**

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**

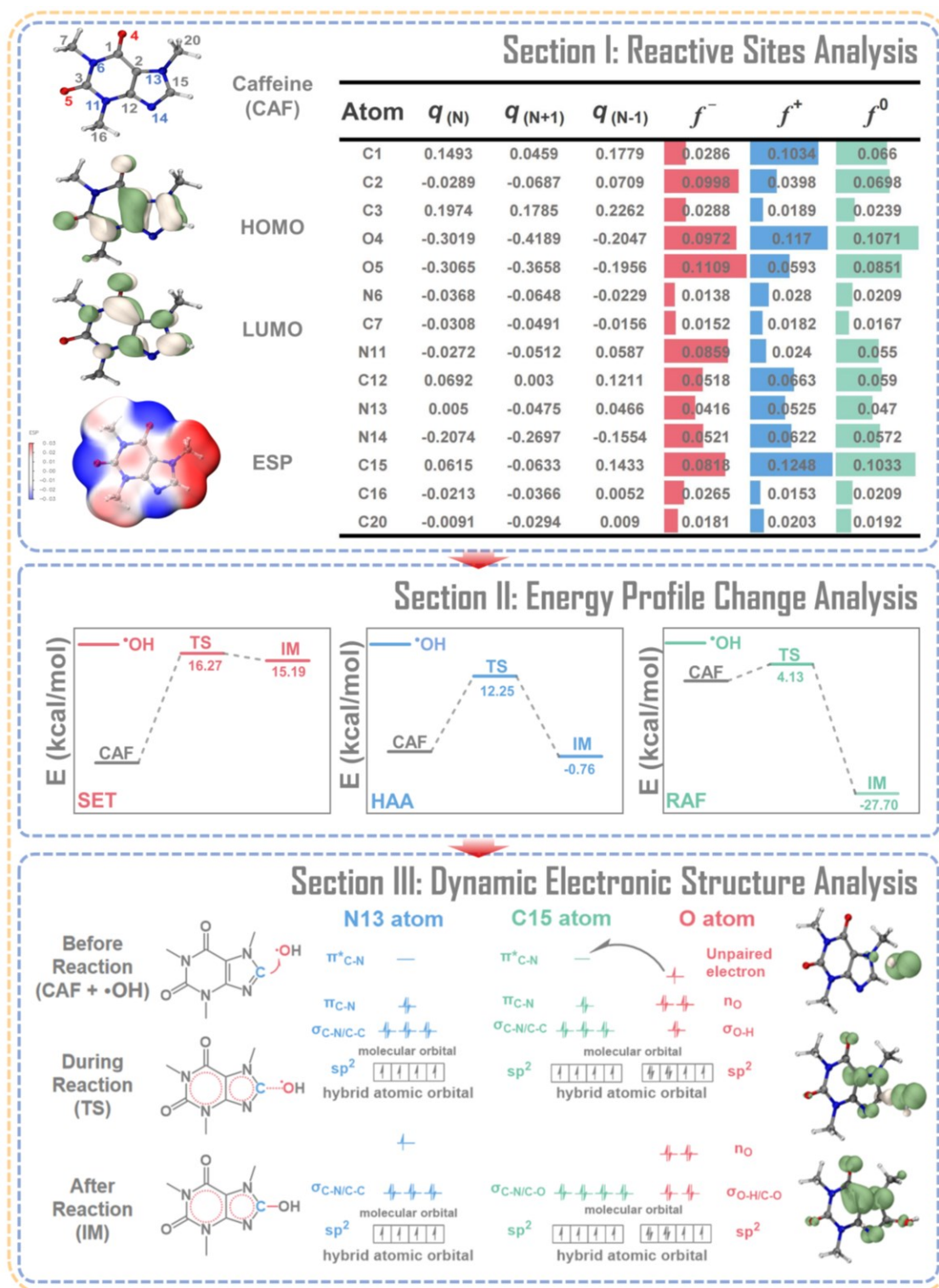
48 **Figure 1** presents an overall framework for environmental theoretical calculation  
49 involving a non-periodic system. The reaction system for contaminant removal (especially  
50 organic contaminant degradation) is the most important non-periodic system considered in  
51 environmental research. 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].



67

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

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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 ( $\omega$ ) 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 ( $\mu$ ) and chemical hardness ( $\eta$ ) 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  $\omega$  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 ( $\Delta G$ ), calculated as the difference  
133 between the products and reactants of elementary processes; and activation energy ( $\Delta G^\ddagger$ ),  
134 calculated as the difference between TS and reactant for RAF and HAA routes. The value of  
135  $\Delta G^\ddagger$  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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## 189 **Declaration of interests**

190 No interests are declared.

191

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