

Unified Rate Theory of Electrochemistry and Electrocatalysis: Fixed Potential Formulation for General, Electron Transfer, and Proton-Coupled Electron Transfer Reactions

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Abstract

Atomistic modeling of electrocatalytic reactions is most naturally conducted within the grand canonical ensemble (GCE) which enables fixed chemical potential calculations. While GCE has been widely adopted for modeling electrochemical and electrocatalytic thermodynamics, the electrochemical reaction rate theory within GCE is lacking. Molecular and condensed phase rate theories are formulated within microcanonical and canonical ensembles, respectively, but electrocatalytic systems described within the GCE require extension of the conventionally used rate theories for computation reaction rates at fixed electrode potentials. In this work, rate theories from (micro)canonical ensemble are generalized to the GCE providing the theoretical basis for the computation reaction rates in electrochemical and electrocatalytic systems. It is shown that all canonical rate theories can be extended to the GCE. From the generalized grand canonical rate theory developed herein, fixed electrode potential rate equations are derived for i) general reactions within the GCE transition state theory (GCE-TST), ii) adiabatic curve-crossing rate theory within the empirical valence bond theory (GCE-EVB), and iii) (non-)adiabatic electron and proton-coupled electron transfer reactions. The rate expressions can be readily combined with *ab initio* methods to study reaction kinetics reactions at complex electrochemical interfaces

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as a function of the electrode potential. The theoretical work herein provides a single, unified approach for electrochemical and electrocatalytic kinetics and the inclusion of non-adiabatic and tunneling effects in electrochemical environments widening the scope of reactions amenable to computational studies.

Keywords: charge transfer, Tafel slope, electrochemical kinetics, Marcus theory, grand canonical

1. Introduction

Electrochemical reactions and especially electrocatalysis are at the forefront of current green technologies. Electrocatalytic conversion of small molecules to fuels, energy and useful chemicals are key components of a sustainable future. To realize and utilize the full potential of electrocatalysis, selective and active catalysts are needed for various applications and reactions including *e.g.* oxygen and hydrogen reduction/evolution reactions, nitrogen reduction to ammonia and CO₂ reduction.[1] Electrochemical conversion of small molecules is most often based on successive proton-coupled electron transfer (PCET), electron transfer (ET), and proton transfer (PT) reactions; the unique aspect of electrocatalysis is the ability to control PCET, ET, and PT kinetics and thermodynamics by the electrode potential.

Rational design of better electrocatalysts working under complex electrochemical environments needs insight from experiments, computational methods as well as theoretical approaches.[1] Experimental techniques have reached certain maturity and tools such as potential sweep and step methods, spectroelectrochemistry, and impedance spectroscopy are standard tools for understanding electrocatalytic reactions.[2] However, a similar level of maturity has not yet been reached within the computational and theoretical electrochemistry communities. Currently, there are several competing but often overlapping computational approaches available for studying reactions at electrochemical interfaces.

Experimentally electrocatalysis is controlled by the electrolyte and electrode potential. To translate these to computationally treatable quantities, it is the combination of the electrolyte and electron electrochemical potentials which determine and control the (thermodynamic) state of electrochemical systems. Therefore, an atomic-level computational model needs to provide an explicit control and description of these chemical potentials as depicted

29 in Figure 1. In statistical thermodynamics fixing the chemical potentials is
30 achieved *via* a Legendre transformation from a canonical ensemble to a grand-
31 canonical ensemble (GCE) for both electrons and nuclei[3] Then, chemical
32 potentials are fixed while particle numbers are allowed to fluctuate.

33 This calls for theoretical and computational approaches within the grand-
34 canonical ensemble (GCE) in which chemical potentials are fixed while par-
35 ticle numbers are allowed to fluctuate. In electronic structure calculations
36 as applied to electrochemical systems one of the largest difficulties is in-
37 deed modelling systems at constant electrode potentials rather than con-
38 stant charges; this corresponds to a change from a fixed particle canonical
39 ensemble to an open, fixed (electro)chemical potential ensemble. This is a
40 rather drastic difference and almost all electronic structure codes work ex-
41 clusively for fixed charge calculations. Another difficulty faced in simulating
42 electrochemistry is the presence of several time- and length-scales taking part
43 in the processes. Very short time and small length-scales are needed when
44 modelling charge transfer and chemical reactions which call for a quantum
45 mechanical treatment of the electrode and reactants. On the other hand,
46 the liquid electrolyte and formation of the electrochemical double-layer need
47 a statistical treatment over a long time to properly represent the electrified
48 solid-liquid interface. The charge distribution at the interface is controlled
49 by the electrode potential which also directly changes both reaction kinetics
50 and thermodynamics.

51 The theoretical basis for fixed potential electronic structure calculations
52 was developed by Mermin who formulated electronic density functional theory
53 (DFT) within GCE.[4, 5]. Later, the GCE-DFT has been generalized
54 to treat nuclear species both classically or quantum mechanically [3, 6–9].
55 The GCE-DFT provides a fully DFT, atomistic approach for computing free
56 energies of electrochemical and electrocatalytic systems at fixed electrode
57 and ionic/nuclear chemical potentials.[3] Importantly, the free energy from
58 a GCE-DFT calculation is in theory exact and unique to a given external
59 potential. In practice, the (exchange-)correlation effects in both quantum
60 and classical systems need to be approximated.

61 Atom-scale modeling of electrocatalytic reactions at fixed electrode[3, 10–
62 20] and ion potentials[3, 12, 14] at electrochemical interfaces has been greatly
63 advanced during the last 10-15 years and utilized in large scale studies of re-
64 actions at electrode surfaces. The work in the field of atomistic modelling
65 of electrocatalytic reactions has been on almost exclusively focused on elec-
66 trocatalytic thermodynamics. Based on the large number of theoretical and

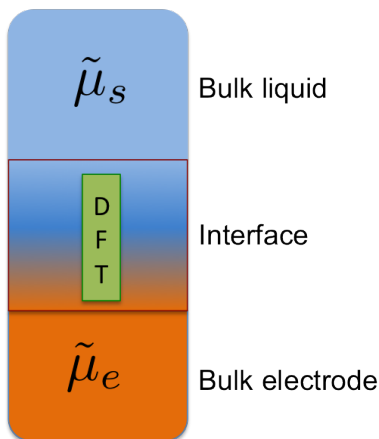


Figure 1: Pictorial model of a proper electrochemical interface at fixed electron $\tilde{\mu}_e$ and solvent/electrolyte $\tilde{\mu}_s$ chemical potentials the atomic level.

67 computational works utilizing GCE-DFT, the framework for thermodynam-
 68 ics within GCE seems generally accepted.

69 However, computation of electrochemical kinetics from atomistic simula-
 70 tions has remained more elusive. Like the electrochemical thermodynamics,
 71 also the kinetics should be computed at fixed electrochemical potentials. This
 72 calls for generalization of fixed particle number canonical rate theories to the
 73 fixed potential GCE. Surprisingly, a general GCE rate theory has not yet been
 74 established; mending this deficiency is the central goal of the present work.
 75 As discussed in detail below, the GCE rate theory must facilitate computa-
 76 tion of rate constants for general chemical reactions and especially PCET,
 77 ET, and PT at fixed chemical potentials. Furthermore, the theory must be
 78 applicable to both inner-sphere and adiabatic as well as outer-sphere, non-
 79 adiabatic and tunneling reactions at constant potentials. In fact, the lack
 80 of generally applicable kinetic models to treat non-adiabaticity and tunnel-
 81 ing in electrocatalytic ET, PT, and PCET under fixed potential situations
 82 limits the scope computational and theoretical investigations of reactions
 83 to adiabatic inner-sphere reactions - a very limited subset of electrochemi-
 84 cal and electrocatalytic reactions. This current restriction is caused by the
 85 absence of theoretical and computational methodologies[21]; while thermo-
 86 dynamics and kinetics of simultaneous PCET reactions are easy to evaluate
 87 for fully adiabatic inner-sphere reactions using (grand) canonical DFT and
 88 (harmonic) transition state theory (TST) *vide infra*, decoupled PCET reac-
 89 tions, outer-sphere ET/PT and non-adiabatic PCET reactions require more

90 advanced methods.

91 In general, ET, PT, and PCET reactions may exhibit both vibronic and
92 electronic non-adiabaticity as well as hydrogen tunneling. The importance
93 and contribution of non-adiabaticity and tunneling may also depend on the
94 the electrode potential.[22, 23] There are several reactions where decou-
95 pled PCET *i.e.* separate ET and PT steps, hydrogen tunneling and non-
96 adiabaticity have been observed. For example, in alkaline ORR pure ET
97 has been proposed as the rate determining step[21, 24–26]. Furthermore, re-
98 cent experiments of ORR on carbon-based materials show conclusively that
99 ET is the rate- and potential-determining step.[27, 28]. On the other hand,
100 solution pH can alter the reaction mechanism and ,*e.g.*, CO₂ reduction can
101 proceed through simultaneous PCET in acidic and through decoupled PCET
102 (ET-PT) in alkaline solutions[29, 30]. It has also been shown that only the
103 inclusion of vibronic non-adiabaticity in electrochemical hydrogen evolution
104 reaction can explain experimentally observed Tafel slopes and kinetic iso-
105 tope effects.[22] There is also experimental evidence that room-temperature
106 hydrogen tunneling takes place during ORR Pt and at low over-potentials
107 tunneling is the prevalent reaction pathway.[23] Kinetics of ET are needed
108 to describe both pure ET and decoupled PCET and in general it is expected
109 that these pathways may prevail on weakly bonding electrode surfaces in
110 oxygen, CO₂, CO, alcohol *etc.* reduction reactions.[31] In fact, PCET re-
111 actions are often vibronically and/or electronically non-adiabatic[32], even
112 under electrocatalytic conditions[22].

113 Even though a general GCE rate theory is missing, schemes for computing
114 rates or energy barriers of adiabatic reactions at constant electrode poten-
115 tials have started to emerge. In some cases reaction barriers have been cal-
116 culated explicitly at a given electrode potentials using GCE-DFT[12, 20, 33–
117 35]. However, more often various correction schemes to (Legendre) trans-
118 form constant charge calculations to GCE are used for studying reaction
119 kinetics.[11, 19, 36–39]. From both approaches the grand energy potentials
120 as a function of the electrode potential or along the reaction coordinate are
121 often found to exhibit quadratic dependence. This quadratic dependence of
122 the grand energy as a function of the potential has been used to transform
123 canonical DFT barriers and reaction energies to grand energies. Recently, it
124 has been noticed that reaction barriers as a function of the potential follow
125 a "Marcus-like" [20] or Brønsted-Evans-Polanyi (non)-linear[38] free energy
126 relations. Other approaches for computing electrode potential-dependent
127 barrier have relied on Butler-Volmer -type (BV) expressions where the bar-

rier has a simple form $G(\eta) = G(\eta = 0) + \alpha\eta$ where η is the over-potential and $\alpha \in [0, 1]$ is the BV symmetry factor.[38, 40, 41]. Independent of the scheme used for obtaining a constant potential reaction barrier, TST-like expressions has been used to compute rate without a sound theoretical basis for the validity of GCE-TST.

Even if GCE-TST proved to be valid (as it does based on the work herein), non-adiabatic and tunneling effects in ET, PT, and PCET effects would be omitted in the fully adiabatic treatments with classical nuclei described above. While neglecting these effects may be reasonable for many electrocatalytic reactions, all electrocatalytic reactions are certainly not inner-sphere nor adiabatic as was discussed. A handful computational and theoretical studies[22, 24, 42–48] at the electronic structure level have studied non-adiabaticity or tunneling effects in electrocatalytic ET/PCET. These pioneering studies utilized simplified model Hamiltonians and wave functions and computation of non-adiabatic/tunneling effects in electrocatalytic reactions. However, using general first principles methods for addressing ET/PCET kinetics have remained elusive thus far. Past theoretical and computational work on non-adiabatic electrochemical ET and PCET rates at a given electrode potentials have been accomplished using either Dogonadze-Kuznetsov-Levich[49, 50], Schmickler-Newns-Anderson[51, 52], or Soudackov-Hammes-Schiffer[22, 32, 45, 53–55] methods. In these treatments the electrode potential is treated as an external parameter modifying the reaction energy or barrier. These models can also incorporate electrostatic interactions between the electrode and the reactant in the double-layer. When combined with first principles simulations, the electronic structure, orbitals, or density of states are computed once for a fixed number of electrons. Then, the electrode potential serves to role of changing the Fermi-level of this static electronic structure. In such calculations the electronic structure itself is considered unaltered when the potential is changed. While this might be valid in some cases, in general the electrode potential changes the solvent structure, bonding of reactants, double-layer, electronic density of states, overlap integrals *etc.* limiting the applicability of the static picture. Instead, modern fixed potential first-principles methods explicitly incorporate the effect of electrode potentials on the interfacial properties and bonding. Another inherent limitation occurring in previous work addressing non-adiabaticity in ET is the limitation to a single orbital picture. The traditional models assume transitions between different electrode single electron states and redox-levels of the molecule to be independent. Technically, achieving this

166 requires separating the total wave function to filled/empty and localized or-
167 bitals. An inherent problem encountered is that this wave function separation
168 cannot be achieved without additional assumptions as shown in Appendix
169 A. In practice this hampers the computation of ET rates from DFT or
170 wave function methods because an additional (and rather) arbitrary orbital
171 separation/localization step is required.

172 A general electrocatalytic rate theory should not be restricted to model
173 (single-orbital) wave functions or Hamiltonians. Instead, a many-electron
174 wave function obtained using *ab initio* methods at a fixed potential should
175 be used to capture the inherent complexity reactions at electrochemical in-
176 terfaces. In the canonical ensemble, ET and PCET rates of electronically
177 and vibronically (non-)adiabatic reactions can be studied using either model
178 or general Hamiltonians[32, 54–60]. Extending these canonical rate theories
179 to fixed potential GCE is the direction pursued herein. This is important
180 from both practical and conceptual point of views that electronic and vi-
181 bronic non-adiabaticity and tunneling can be included in electrochemical,
182 fixed potential ET, PT and PCET rates using generalized Hamiltonians,
183 many-electron wave functions, and rate theory.

184 The above discussion highlights that electrochemical (outer-sphere) and
185 electrocatalytic (inner-sphere) reactions have treated using different approaches.
186 Commonly, electrocatalytic reactions have been studied using adiabatic TST
187 theory while electrochemical reactions have relied on perturbative non-adiabatic
188 theories. However, in the canonical ensemble, all rate theories equally appli-
189 cable to inner- or outer-sphere reactions can be derived using a single general
190 framework provided by Miller[61–63]. This general theory forms the basis of
191 the extension to grand canonical rate theories of the current work.

192 The importance and impact of the of the general framework in the electro-
193 catalytic context is best appreciated by considering how different rate theories
194 enable description of (electro)catalytic reactions and phenomena. Of course,
195 archetypal adiabatic reactions, including simultaneous adiabatic PCET re-
196 actions, can be studied using the common (harmonic) TST with classical
197 nuclei.[61] The real power of the general rate theories is the ability to ex-
198 tend them to treat reactions where tunneling or non-adiabaticity are impor-
199 tant. Such methods include ring-polymer TST[64–67], path-integral TST[68],
200 semi-classical instanton methods[67, 69], or semi-classical TST[70, 71], for ex-
201 ample. Also non-adiabatic ET and PCET reactions can be modelled within
202 the general framework by using non-adiabatic TST[54, 55, 72–74] which at
203 the classical limit gives a Marcus-type equation[75] for the barrier and a

204 non-adiabatic correction for the transmission coefficient can be included.

205 The goal of the present work is to formulate a general rate theory for
206 reactions taking place at fixed (electro)chemical potentials. The formula-
207 tion is equally applicable to electrocatalytic and electrochemical reactions
208 and, hence, presents a general unified approach. This includes the possibility
209 to account for tunneling as well as vibronic and electronic non-adiabaticity.
210 While methods for treating thermodynamics, locating transition states and
211 energy barriers within GCE have been devised, a general method for com-
212 putation reaction rates – not just barriers – is not yet available. Here this
213 is obtained by extending general (micro)canonical rate theories to electro-
214 chemical systems using a GCE formulation developed herein. The GCE rate
215 theory enables the use of all canonical rate theories in constant potential
216 simulations.

217 In this work, the general framework is developed and utilized to derive
218 rate constants for adiabatic ET and PCET reactions using a generalized
219 GCE Marcus-like [75] empirical valence bond theory (GCE-EVB). The non-
220 adiabatic ET and PCET rate constants are derived using a golden-rule for-
221 malism within GCE. The theoretical work results in ET and PCET rate con-
222 stants valid for both adiabatic and non-adiabatic (proton-coupled) electron
223 transfer rates and the inclusion of proton tunneling in PCET. The developed
224 rate theories can readily be combined with modern computational methods
225 based on (GCE-)DFT. The derived rate equations form the basis for treat-
226 ing electrocatalytic kinetics and combining them with (GCE-)DFT methods
227 expands the type of systems, conditions, and phenomena in electrocatalysis
228 amenable for first principles modelling.

229 The paper is organized as follows. In Section 2 a general rate theory
230 and TST within GCE are developed. Rest of the paper focuses on ET and
231 PCET kinetics using GCE-TST. Section 3 shows how the adiabatic barrier
232 and rate of ET and PCET reactions are computed using GCE-EVB and free
233 energy perturbation theory within GCE leading to a fixed potential version
234 of Marcus theory. Tafel slopes and other use quantities as extracted from
235 GCE-EVB are analyzed. Finally, in section 4 non-adiabatic rate constants
236 for ET and PCET reactions with generalized first-principles Hamiltonians
237 and many-electron wave functions.

238 **2. Rate theory in the grand canonical ensemble**

239 As highlighted in the preceding discussion, the electrode potential is ex-
240 pected to affect the energetics and kinetics in complex ways. Thus, the poten-
241 tial should be treated explicitly rather than as a simple corrective parameter
242 as often done in theoretical and computational models used in electrocatal-
243 ysis. Formulating all expectation values within GCE naturally includes the
244 electrode potential from the start and this forms the basis for the methods de-
245 veloped here and building on our previous grand canonical multi-component
246 DFT[3]. The key is that the electrode potential is included in the *ab initio*
247 Hamiltonian within the GCE and as results all observables and quantities
248 depend explicitly on the potential. For details on GCE, see Appendix B and
249 previous work in Ref.3.

250 To extend (micro)canonical rate theory to the GCE, only particle con-
251 serving reactions are considered. Thus, only a state with N particles can
252 be converted to state with N particles but the population and probability
253 of N particle states is determined by the GCE density operator. Hence,
254 all equilibrium quantities are always well-defined but jumps between states
255 with unequal number of particles are suppressed. In general this is not ex-
256 pected to limit the applicability of the rate expressions derived in this work;
257 if a quantum system is characterized by particle conserving operators (\hat{H}
258 Hamiltonian, \hat{S} entropy, and \hat{N} particle number), even time-dependent ob-
259 servables are obtained as ensemble weighted expectation values from $O(t) =$
260 $\text{Tr} \left[\hat{\rho} \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0) \right] = \sum_n p_n \langle \psi_n | \hat{U}(t_0, t) \hat{O}(t) \hat{U}(t, t_0) | \psi_n \rangle$ which do not
261 include changes between states with different number of particles.[76] Hence,
262 even explicit propagation of the wave function does not allow sudden jumps
263 in particle numbers or jumps between states between different number of
264 particles.

265 In a similar way, particle fluxes needed for the flux formulation of rate
266 theory (see below) can be applied within the GCE as long as (local) equilib-
267 rium is maintained. This implies that the Hamiltonian is time-independent
268 and that only particle conserving reactions contribute to the rate constant
269 according to the grand canonical distribution[77]. Furthermore, computation
270 of correlation functions and hence fluxes poses both theoretical and computa-
271 tional difficulties. While both may in principle be directly computed within
272 GCE[77], the computation includes the coupling of the system to the par-
273 ticle reservoir and introduces the reservoir time scales. Also, the sampling
274 needs to account for trajectories for which the particle number is equal at

275 times t and $t + \tau$. This is because in GCE the phase space volume is not
 276 globally conserved and Liouville theorem does not hold. As a result, the
 277 computed ensemble properties will depend on time if the system is not in
 278 equilibrium i.e. the phase distribution function $\rho(\mathbf{q}, \mathbf{p}, N, t)$ is not stationary
 279 i.e. if $d_t \rho(\mathbf{q}, \mathbf{p}, N, t) \neq 0$ [77–79] (\mathbf{p} and \mathbf{q} are momentum and position, re-
 280 spectively). In the context of the present work it is important to notice that
 281 both equilibrium ($d_t \rho(\mathbf{q}, \mathbf{p}, N, t) = 0$ at $t \rightarrow \infty$) and instantaneous ($\lim_{t \rightarrow 0^+}$)
 282 properties are uniquely defined by the GCE[77, 79]; both qualities are abso-
 283 lutely essential in order to formulate the rate and transition state theories
 284 within GCE.

285 Herein only equilibrium and instantaneous quantities are used. Interme-
 286 diate times would require running GCE-dynamics or making assumptions on
 287 the reservoir-system couplings. Hence, non-equilibrium processes cannot be
 288 treated using the approaches presented in this paper. Another limitation of
 289 the current approach is that kinetics of electron transfer from the electron
 290 "bath" degrees of freedom are not included and are therefore assumed suffi-
 291 ciently fast. Neither of these limitations are not expected greatly limit the
 292 applicability of the approach for electrocatalytic or electrochemical reactions.
 293 In these reactions the electron bath is provided by a conducting electrode and
 294 equilibrium conditions are controlled by constant temperature and potential
 295 which also provide the natural control parameters in the GCE utilized in
 296 this work. It is noted that mass transfer in electrochemical systems is not in
 297 equilibrium or even steady-state. However, the reaction rate coefficients are
 298 independent of particle fluxes and concentrations and therefore the elemen-
 299 tary rate constants can be characterized by their equilibrium values as long
 300 as the Hamiltonian of the quantum part is time-independent and particle
 301 conserving.

302 After establishing the particle conserving and equilibrium nature of the
 303 rate constants, the GCE rate constants can be formulated. To allow vari-
 304 ous types of reactions to be described, the canonical rate expression due to
 305 Miller[61–63, 69] is used:

$$k(T, V, N)Q_I = \int dE P(E) \exp[-\beta E] \quad (1)$$

306 where $P(E)$ is the transition probability at a given energy, Q_I is the
 307 canonical partition function of the initial state, and $\beta = (k_B T)^{-1}$. This
 308 formulation can be expressed in several equivalent forms and below these
 309 different flavors are referred to as the flux correlation formulation.[62]. Im-

310 posing the particle conservation of wave functions and equilibrium lead to
 311 grand canonical reaction rate of the form[62, 72]

$$\begin{aligned}
 k(T, V, \mu)\Xi_I &= \sum_{N=0}^{\infty} \exp[\beta\mu N] Q_0(T, V, N) k(T, V, N) \\
 &= \sum_N \exp[\beta\mu N] \int dE P(E) \exp[-\beta E] \\
 &= \sum_{N=0}^{\infty} \exp[\beta\mu N] \lim_{t \rightarrow \infty} C_{fs}(t)
 \end{aligned} \tag{2}$$

312 where $\Xi_I = \exp[\beta\mu N] Q_I$ is the initial state grand partition function and
 313 where $C_{fs}(t)$ is either the quantum or classical flux-side correlation function
 314 in the canonical ensemble, see below. Above N is the number of species
 315 (nuclear or electronic) in the system. Based on the discussion above, only
 316 the $t \rightarrow 0^+$ and $t \rightarrow \infty$ should be considered for the flux-side correlation
 317 function in the rate expressions.

318 While the above equations are completely general and various flavors of
 319 rate theories can be extracted by invoking different Hamiltonians and transi-
 320 tion probabilities, they are somewhat cumbersome to treat. Indeed, it would
 321 be convenient if the GCE could be used directly to evaluate the rate without
 322 explicitly sum over different particle numbers. Moving towards but still re-
 323 taining maximum generality, it is assumed that the nuclei follow classical tra-
 324 jectories. While this might seem like a drastic assumption, Feynman[80] has
 325 shown that quantum mechanics can be formulated using classical trajectories
 326 as long all possible paths are included. Indeed, the use of Feynman's path
 327 integral methodology is behind several quantum mechanical rate theories[81].
 328 Using a classical Hamiltonian and suppressing non-adiabatic effects by using
 329 a a single potential energy surface (PES), the flux-side correlation can be
 330 written in the ring-polymer form as[81]

$$C_{fs}(t) = \frac{1}{(2\pi\hbar)^f} \int d\mathbf{p}^f d\mathbf{q}^f \exp(-\beta_n H_n) \delta[f(\mathbf{q})] \dot{\mathbf{q}} h[f(\mathbf{q}_t)] \tag{3}$$

331 where n is the number of beads, $\beta_n = \beta/n$, $f = Nn$, $H_n = \sum_{i=1}^N \sum_{j=1}^n \frac{|\mathbf{p}_{i,j}|^2}{2m_i} +$
 332 $\frac{1}{2} |\mathbf{q}_{i,j} - \mathbf{q}_{i,j-1}|^2 + \sum_{i=1}^n V(q_{1,i} \dots N, i)$. Above, $\delta[f(\mathbf{q})]$ constrains the trajecto-

333 ries to start from the dividing surface, $\dot{\mathbf{q}}$ is the initial flux along the reaction
 334 coordinate, and $h[f(\mathbf{q}_t)]$ is the side function which includes the dynamic in-
 335 formation whether a trajectory is reactive or not. Also, the non-adiabatic
 336 reactions can be described using a Hamiltonian with several coupled PESs
 337 and by using side function h which projects the state on different PESs.
 338 [82, 83]. At the classical limit $T \rightarrow \infty$ and $\beta_n \rightarrow 0$ leads to the shrinkage
 339 of the ring-polymer to a single bead. At this limit $C_{fs}(t)$ obtains its cor-
 340 rect classic limit. In principle, $C_{fs}(t)$ within GCE can be directly computed
 341 with nuclear quantum and non-adiabatic effects using ring polymer molecular
 342 dynamics[84] but this is not within the scope of the present work.

343 Next transition state theory (TST) assumption is made[61–63]. In TST,
 344 the instantaneous $\lim_{t \rightarrow 0_+} C_{fs}(t)$ is considered corresponding to the assump-
 345 tion that there are no-recrossings of the dividing surface. Note that TST
 346 in this form is valid for non-adiabatic reactions as well if several PESs are
 347 used for computing C_{fs} . While a general, rigorous quantum TST has proven
 348 difficult to obtain due to the non-commuting nature of the flux and Hamilto-
 349 nian operators, recent work has shown that the zero-time dynamics lead to
 350 ring-polymer TST which can be considered as a quantum TST.[65, 66] Fur-
 351 thermore, the path integral QTST[68] and its harmonic approximation (the
 352 popular semi-classical instanton rate theory in its ring polymer form[67, 85])
 353 also arise from the path integral presentation of quantum mechanics. Both
 354 quantum/classical and adiabatic/non-adiabatic TSTs are written as

$$k_{TST}(T, V, N)Q_0(T, V, N) = \lim_{t \rightarrow 0_+} C_{fs}(t) \quad (4)$$

355 and the exact rate is recovered by introducing a correction

$$k(T, V, N) = \lim_{t \rightarrow \infty} \kappa(t)k_{TST}(T, V, N) \quad (5)$$

$$\text{with } \kappa(t) = \frac{C_{fs}(t)}{C_{fs}(t \rightarrow 0_+)}$$

356 where $\kappa(t)$ is the time-dependent transmission coefficient. For long-times,
 357 it can also be written as $\kappa = k(T, V, N)/k_{TST}(T, V, N)$. [86] Inserting this
 358 equation in Eq.(2) can be used to compute the most general grand canonical
 359 rate constant.

360 The above treatment is very general and needs further simplification to
 361 enable facile computation of reaction rates within the GCE. Here I will con-

362 concentrate only on classical nuclei and then instead of working with the flux-
 363 side correlation function it is easier to write the rate in terms of the cu-
 364 mulative reaction probability of Eq. (2). For classical nuclei, the general
 365 rate equation in the GCE is written in terms of the time-integral of the
 366 flux correlation function which contains all the dynamic information[62, 63]:

$$367 \quad P_r(\mathbf{p}, \mathbf{q}) = \lim_{t \rightarrow \infty} h[f(\mathbf{q}_t)] = \int_0^\infty dt \frac{d}{dt} h[f(\mathbf{q}_t)] = \int_0^\infty dt C_{ff}(\mathbf{q}_t, \mathbf{p}_t).$$

$$\begin{aligned} k(T, V, \mu) \Xi_I &= \sum_{N=0}^{\infty} \exp[\beta \mu N] \int dE P_d(E) \exp[-\beta E] \\ &= \sum_{N=0}^{\infty} \exp[\beta \mu N] \int \frac{d\mathbf{p} d\mathbf{q} \exp[-\beta H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) P_r(\mathbf{p}, \mathbf{q})}{(2\pi\hbar)^N} \\ &= \sum_{N=0}^{\infty} \exp[\beta \mu N] \int \frac{d\mathbf{p} d\mathbf{q} \exp[-\beta H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) \int_0^\infty dt C_{ff}(t)}{(2\pi\hbar)^N} \quad (6) \\ &\approx \sum_{N=0}^{\infty} \exp[\beta \mu N] \frac{k_B T}{h} Q^\ddagger \int dt \delta(t) = \sum_N \exp[\beta \mu N] \frac{k_B T}{h} Q^\ddagger \\ &\equiv \frac{k_B T}{h} \Xi^\ddagger \end{aligned}$$

368 where on the second last line making the short time approximation[63]
 369 to $C_{ff}(t \rightarrow 0) = \frac{k_B T}{h} Q^\ddagger \delta(t)$ leads to the TST expression. Above, $P_d(E)$ de-
 370 notes transition probability for classical nuclei but the electrons are of course
 371 quantum mechanical[59, 72]. The result on the last line of the previous equa-
 372 tion, shows that the structure of GCE-TST and canonical TST have similar
 373 structures. A similar conclusion was also derived by Chandler in Ref.87 if
 374 memory effects are neglected. To obtain the GCE rate constant without in-
 375 voking the TST approximation one can use the transmission coefficient to
 376 write

$$k(T, V, \mu) \Xi_I = \sum_{N=0}^{\infty} \exp[\beta \mu N] \kappa(T, V, N) \frac{k_B T}{h} Q^\ddagger \approx \langle \kappa_\mu \rangle \frac{k_B T}{h} \Xi^\ddagger \quad (7)$$

377 where it is assumed that the transmission coefficient is insensitive to
 378 changes in the particle number and $\langle \kappa_\mu \rangle$ is the effective transition proba-
 379 bility. To complete the derivation for the classical GCE rate constant, the
 380 rate is expressed in terms of grand energies

$$\begin{aligned}
k(T, V, \mu) &= \langle \kappa_\mu \rangle \frac{k_B T}{h} \exp[-\beta(\Omega^\ddagger - \Omega_I)] \\
&= \langle \kappa_\mu \rangle \frac{k_B T}{h} \exp[-\beta\Delta\Omega^\ddagger]
\end{aligned}
\tag{8}$$

381 where the definition $\Omega_i = -\ln(\Xi_i)/\beta$ has been used. Above the only new
382 assumption besides grand canonical equilibrium distribution and the TST,
383 is that the flux out of the transition state does not depend on the number
384 of particles in the system. For large enough systems and small variations
385 in the particle this a well justified assumption. What is achieved is a fixed
386 chemical potential rate equation where the rate is determined by the grand
387 free energy barrier. The transmission coefficient needs to be approximated
388 but this depends on the case at hand. The harmonic GCE-TST expression
389 for the fully open system is derived in Appendix C resulting in Eq (C.4).

390 *2.1. Allowing only the electron number to fluctuate*

391 The general development above is valid when both nuclear and electronic
392 subsystems are open. A significant simplification results if the number of nu-
393 clei is not allowed to fluctuate and the system is open only for electrons. This
394 is also the typical scheme used in first principles modelling within GCE. Har-
395 monic TST rates for constant number of nuclei and constant electrochemical
396 potentials are derived in Appendix C.

397 Fixing only the electron chemical potential gives a semi-grand canonical
398 ensemble used for deriving the thermodynamics of electrocatalytic system in
399 Ref. 3. Using the same semi-GCE to kinetics, is used herein to derive rate
400 equations as a function of electrode potential. *From now on, only the numbers*
401 *of electrons is allowed to fluctuate and the state of the system is determined*
402 *by T , V , number of nuclei N_N , chemical potential of the electrons μ_n , and*
403 *number of electrons in the system N unless explicitly specified otherwise.*

404 **3. Adiabatic barriers and rates from GC-EVB**

405 To compute the GCE-TST rate at some electrode potential, the grand
406 energy barrier of Eq. (8) needs to be obtained. For adiabatic reactions
407 methods like the constant-potential[20] nudged elastic band[88] can be used.
408 However, usually one is interested in rates as a function of the electrode
409 potential and, hence, the barriers needs to be obtained for a range of electrode

410 potentials which is computationally expensive. Another possibility is for
 411 computation of the grand energy barrier, is to extend the adiabatic Marcus
 412 theory[75] to the GCE. Marcus theory can be viewed as special case of the
 413 empirical valence bond (EVB) theory[89] commonly utilized in electron[75]
 414 and proton transfer theories.[53, 89–92]. As shown below, the GCE-EVB
 415 theory has the advantage, that the adiabatic barrier needs to be explicitly
 416 computed only for at a single electrode potential. Barriers at other potentials
 417 can be obtained using well-defined interpolation of Eq.(22).

418 In these EVB and Marcus theories the initial and final states are pre-
 419 sented using diabatic states, effective wave functions and free energies[75].
 420 This can be extended to GCE by using two effective, fixed potential surfaces
 421 which can be understood as a statistical mixture of states with probabilities
 422 given by the density operator in GCE (see Appendix B and our previous
 423 work in 3). Importantly, the diabatic ground states obtained using the GCE
 424 density operator naturally include many-body states of coupled electrode-
 425 reactant-solvent system and the complexity of the electrochemical interface
 426 is implicitly included in the model. Also, there is no need to decompose the
 427 rate constants to orbital dependent quantities; in the current GCE formu-
 428 lation, the redox-molecule and the electrode are fully coupled and the total
 429 wave function $|r, \mathbf{e}\rangle$ is treated as a single entity in (see Appendix A for ad-
 430 ditional discussion). Then, two grand canonical diabatic all-electron wave
 431 functions are used to form an effective diabatic GCE Hamiltonian. This is
 432 analogous to molecular Marcus theory in which the canonical diabatic Hamil-
 433 tonian comprises of an initial (oxidized) I and final(reduced) molecule F .

434 To form the GCE diabatic states, the work of Reimers[93, 94] on canonical
 435 ensembles is followed. As noted by Reimers, the density matrix $\hat{\rho}$ can be
 436 written using either adiabatic or non-adiabatic states. Especially, when only
 437 two electronic states are used, the connection of the Born-Huang expansion
 438 bears striking resemble to the commonly used 2×2 diabatic Hamiltonians
 439 used for deriving electron transfer rate theory. In the canonical ensemble,
 440 the diabatic states are ϕ_I and ϕ_F corresponding to the electron localized
 441 on the initial (I) or final (F) state while the molecular electronic-vibrational
 442 Hamiltonian is

$$H_{dia}(N, V, T) = \begin{bmatrix} H_{II} & H_{IF} \\ H_{FI} & H_{FF} \end{bmatrix} \quad (9)$$

443 with

$$H_{II}(R) = \langle \phi_I | \hat{H}_{el}(R) | \phi_I \rangle + \hat{T}_{nuc} = E_I + \hat{T}_{nuc} \quad (10a)$$

$$H_{FI}^* = H_{IF} = \langle \phi_I | \hat{H}_{tot}(R) | \phi_F \rangle \quad (10b)$$

$$H_{FF} = \langle \phi_F | \hat{H}_{el}(R) | \phi_F \rangle + \hat{T}_{nuc} = E_F + \hat{T}_{nuc} \quad (10c)$$

444 where \hat{T}_{nuc} is the nuclear kinetic energy operator, $\hat{H} = \hat{H}_{el} + \hat{T}_{nuc}$, and H_{el}
 445 includes electron kinetic energy and Coulomb energies of the electron-nucleus
 446 system. The Born-Huang, or vibronic, states are

$$\begin{aligned} \Psi_i(R) &= \sum_j [C_{ij}^I |\psi_I\rangle |\chi_j\rangle + C_{ij}^F |\psi_F\rangle |\chi_j\rangle] \\ &= \sum_{k=I,F} |\psi_k\rangle \sum_j C_{ki,j}^I |\chi_j\rangle \end{aligned} \quad (11)$$

where Ψ , ψ , and χ are the vibronic, electronic, and nuclear wave functions, respectively. C is the weight of each state. Using these definitions the density matrix for a canonical ensemble is

$$\rho(N, V, T) = \begin{bmatrix} \rho_{II} & \rho_{IF} \\ \rho_{FI} & \rho_{FF} \end{bmatrix} \quad (12)$$

447 with $\rho_{AB} = \sum_j C_{ji}^A C_{ji}^B$ and the total density matrix has dimension $(2 \times$
 448 $N_i) \times (2 \times N_i)$.

449 Next the diabatic canonical Hamiltonian is generalized to the grand canon-
 450 ical ensemble. To simplify the notation, it is assumed that the initial and
 451 final can approximated as a single electronic state and a single vibrational
 452 state - extension to include more vibrational state is straight-forward. Then,
 453 the total vibronic state is written as $\Psi(\mathbf{R}) \approx c_I |\psi_I\rangle |\chi_I\rangle + c_F |\psi_F\rangle |\chi_F\rangle$. In
 454 electron transfer theory the vibronic states are often assumed to be harmonic
 455 but here such an assumption is not needed. Next, the total number of elec-
 456 trons is allowed to fluctuate while the electron Fermi-level is fixed. These
 457 are effectively introduced by using the equilibrium reduced density operator
 458 within the GCE [3] (see also Appendix B)

$$\hat{\rho}_{red} = \sum_N p_N \sum_{ij} |\Psi_{Ni}\rangle \langle \Psi_{Nj}| \quad (13)$$

$$\text{with } |\Psi_i\rangle = c_I |\psi_I\rangle |\chi_I\rangle + c_F |\psi_F\rangle |\chi_F\rangle$$

459 where p_N is the GCE weight for a state with N electrons. The result-
 460 ing density matrix will have N -dimensional block-diagonal form with 2×2
 461 blocks. Similarly the Hamiltonian matrix is made of Eq.(9) H_{dia}^N blocks. Di-
 462 agonalizing each block separately will give canonical adiabatic states whereas
 463 $\text{Tr} \left[\hat{\rho}_{red} \hat{H} \right]$ gives the adiabatic grand canonical free energy. Because the trace
 464 is cyclic, both $\hat{\rho}_{red}$ and \hat{H} can be reorganized which keeps the (diabatic) free
 465 energy unchanged as long as diagonal elements remain at the diagonal. This
 466 freedom is utilized to reorganize the matrix so that the upper part of $\hat{\rho}_{red}$
 467 and \hat{H} correspond to the initial state and the lower part to the final diabatic
 468 states. Tracing the upper and lower parts separately, diabatic GC free en-
 469 ergies of initial and final states (Ω_{II} and Ω_{FF}) are obtained. The adiabatic
 470 energy is computed by diagonalizing a 2×2 GCE Hamiltonian.

$$H_{GCE-dia} = \begin{bmatrix} \Omega_{II} & \Omega_{IF} \\ \Omega_{FI} & \Omega_{FF} \end{bmatrix} \quad (14)$$

471 where the diagonal elements are the grand energies of the oxidized (II) and
 472 reduced (FF) systems. The off-diagonal elements account for the interaction
 473 and mixing of the initial and final states. As written here, they can be
 474 understood in the framework of empirical valence bond (EVB) theory[89]
 475 commonly utilized in electron[75] and proton transfer theories.[53, 89–92]
 476 In this, way the off-diagonal elements can be fitted so that diagonalization
 477 of Eq.(14) produces the adiabatic grand canonical potential energy surface.
 478 Hence, the above methodology might be called GCE-EVB approach.

479 Finally, note that the (diabatic) grand canonical states correspond to
 480 a single electron density which are guaranteed theory to be unique for a
 481 given electrode potential by the Hohenberg-Kohn-Mermin[3, 4]. The only
 482 disambiguity is the definition of these diabatic states. In principle it is also
 483 possible to add other, possibly excited states as basis states. In practice the
 484 GCE diabatic energies, (Ω_{II} and Ω_{FF}), can be computed directly by applying
 485 using *e.g.* constrained DFT[95–97] with fixed potential DFT. Below it is
 486 shown how the grand canonical free energies can be obtained from atomistic
 487 simulations.

488 3.1. Computation of diabatic GCE surfaces and barriers

489 An approach often used in molecular simulations for constructing the
 490 diabatic free energy curves is to sample the diabatic potentials along a suit-
 491 able reaction coordinate. For ET, PT, and PCET reactions in the canon-

492 ical ensemble this coordinate is the energy gap between the two diabatic
493 states as shown by Zusman[98] and Warshel[99]: $\Delta E_{gap}(R) = E_F(R) -$
494 $E_I(R)$. [78, 100] From the sampled energy gap the free energy curves are
495 obtained as $A(R) = -k_B T \ln(p(E_{gap}(R))) + c$. If the distribution is Gaus-
496 sian ($p(E_{gap}(R)) = c \exp[-(\Delta E_{gap} - \langle \Delta E_{gap} \rangle)^2 / 2\sigma^2]$) and the resulting free
497 energy curves a parabolic. The barrier in EVB or Marcus theory is then ob-
498 tained from the intersection of the initial and final diabatic curves[100–103].
499 Within GCE, the energy cap is simply $E_{gap}(R; \mu) = \sum_{N,i} p_{N,i} E_{gap}(R_i, N)$.
500 The gap distributions can be formulated and computed by generalizing Zwanzig’s[104]
501 the canonical free energy perturbation theory to the GCE. This route pro-
502 vides a rigorous way to derive the reaction barrier in terms of diabatic states
503 and energies as presented in Appendix D.

504 The reaction energy barrier can be computed from the initial-final state
505 energy gap distribution functions using[99, 105–110]

$$k_{IF} = \kappa \frac{\exp[-\beta g_I(\Delta E^\ddagger)]}{\int d\Delta E \exp[-\beta g_I(\Delta E)]} = \kappa p_I(\Delta E^\ddagger) \quad (15)$$

506 where $g_i(\Delta E)$ is the free energy curve in state i as a function of the energy
507 gap, $p_I(\Delta E^\ddagger)$ is the gap distribution at the transitions state, and κ denotes
508 an effective pre-factor. The above shows that the reaction rate is determined
509 by the energy gap distribution function $p^I(\Delta E) = \langle \delta(\Delta E(R) - \Delta E) \rangle_I$ from
510 Eq. (D.6).

511 When assuming that $E_{gap}(R; \mu)$ is Gaussian, the GC-diabatic states are
512 parabolic and the Marcus barrier in GCE is given by Eq. (18). As shown
513 in the Appendix C and Section 4 for the GCE-NATST, the (Gaussian) gap
514 distribution may be derived using a (second order) cumulant expansion. This
515 results in gap distribution of the following form

$$p_I(\Delta E) = \frac{1}{\sqrt{2\pi\sigma_I}} \exp\left[-\frac{(\Delta E - \langle \Delta E \rangle_I)^2}{2\sigma_I^2}\right] \quad (16)$$

516 where $\langle \Delta E \rangle_I$ is the energy gap expectation value in the initial state ob-
517 tained from Eq. (D.6) and $\sigma_I = \langle (\Delta E)^2 \rangle_I - (\langle \Delta E \rangle_I)^2$ is the gap variance.
518 The Marcus relation is then obtain after standard manipulations[100, 106]
519 by inserting these relations in Eq. (D.8) to give

$$p_I(\Delta E^\ddagger) = \frac{1}{\sqrt{4k_B T \Lambda}} \exp\left[-\beta \frac{(\Delta \Omega_{FI} + \Lambda)^2}{4\Lambda}\right] \quad (17)$$

520 where $\sigma_I^2 = \sigma_F^2 = 2k_B T \Lambda = k_B T (\langle \Delta E \rangle_I - \langle \Delta E \rangle_F)$, Λ is the reorganiza-
 521 tion grand energy and $\Delta\Omega_{FI} = \frac{1}{2}(\langle \Delta E \rangle_I + \langle \Delta E \rangle_F)$ is the reaction grand
 522 energy as depicted in Figure 3.1. Finally, the Marcus expression within GCE
 523 is

$$k = \frac{\kappa}{\sqrt{4k_B T \Lambda}} \exp \left[-\beta \frac{(\Delta\Omega_{FI} + \Lambda)^2}{4\Lambda} \right] \quad (18)$$

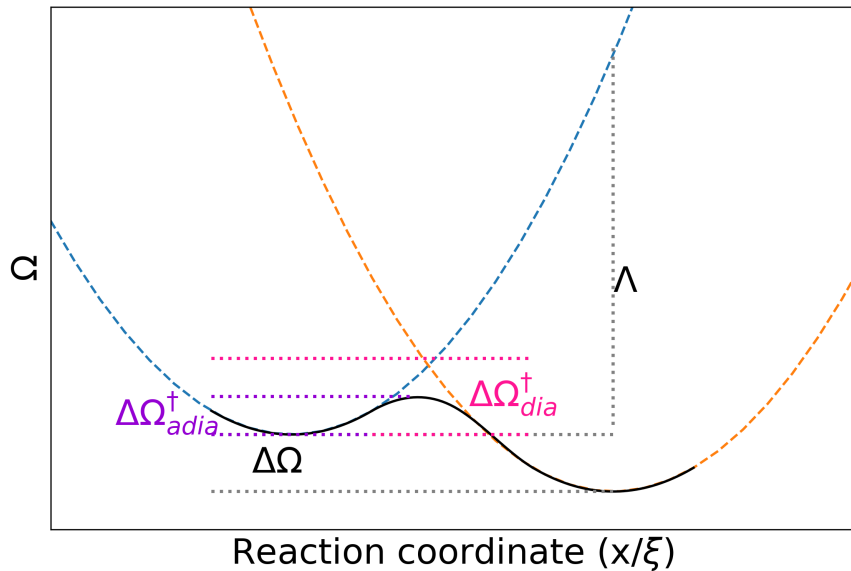


Figure 2: Schematic depiction of the important GCE-EVB quantities. The blue (orange) dashed lines is initial (final) diabatic surface while the black solid line is the adiabatic surface.

524 The energy barrier of Eq. (18) is the diabatic energy barrier. The adi-
 525 abatic barrier can be computed using Eq. (14) as discussed in Section.
 526 3.2 below. One caveat to keep in mind is more involved within the GCE
 527 than the canonical ensemble as shown in Section 4. The above result may
 528 safely be used when $\kappa \approx 1$ for all particle numbers meaning that the reaction
 529 is always fully adiabatic.

530 *3.2. Implications of the canonical GCE-EVB rate theory*

531 For symmetric grand energy surfaces the diabatic grand energy barrier
 532 can be estimated from the crossing point of the two quadratic grand energy
 533 surfaces with equal curvatures is given in Eq. (18). The requirement of equal
 534 curvature can be relaxed following Mattiat and Richardson[74], who compute
 535 the reorganization energies for both the initial and final states Λ_I and Λ_F ,
 536 respectively. Then the asymmetry parameter may be defined as

$$\alpha_{as} = \frac{\Lambda_I - \Lambda_F}{\Lambda_I + \Lambda_F} \quad (19)$$

537 and the transition state is located at the crossing point

$$x^\ddagger/\xi = -\frac{1}{\alpha_{as}} + \frac{1}{\alpha_{as}} \sqrt{1 - \alpha_{as} \left(\alpha_{as} + \frac{4\Delta\Omega}{\Lambda_I + \Lambda_F} \right)} \quad (20)$$

538 Using these definitions the asymmetric diabatic Marcus barrier and rate
 539 are obtained as

$$\Delta\Omega^\ddagger = \frac{1}{4}\Lambda_I (x^\ddagger/\xi - 1)^2 \quad (21a)$$

$$k \approx \frac{\kappa}{\sqrt{4k_B T \Lambda_I}} \frac{1 + \alpha_{as}}{1 + \alpha_{as} x^\ddagger/\xi} \exp[-\beta\Delta\Omega^\ddagger] \quad (21b)$$

540 If $\alpha_{as} \rightarrow 0$, the regular Marcus rate and barrier are obtained. In Fig.3.2
 541 the effect of asymmetry and reaction energy to the reaction barrier and lo-
 542 cation of the transition state are compared. It can be seen that both the
 543 barrier heights and its location are affected by the asymmetry and reaction
 544 energy.

545 The above equations enable a theoretically justified way to compute or
 546 predict the reaction barrier at a given electron chemical potential using just
 547 few parameters: Λ and $\Delta\Omega$. Both the barrier height and shifts in its location
 548 can be determined. Furthermore, it is not necessary to find the transition
 549 state geometry as long as all the parameters can be computed. The practical
 550 computations can be made using *e.g.* fixed potential implementations dia-
 551 batic electronic structure methods such as the constrained DFT[95–97] The
 552 grand energy curves in Figure 3.2 qualitatively reproduce the DFT computed
 553 reaction free energy barriers for HER[20] and CO₂ reduction[38].

554 The adiabatic reaction barrier can be extracted from the non-adiabatic
 555 barrier obtained by diagonalizing Eq.(14) or from .(18) by introducing an

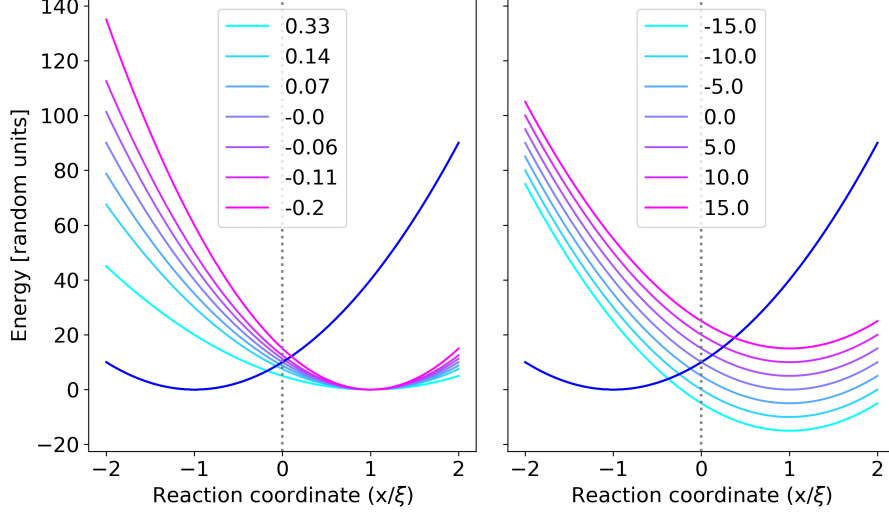


Figure 3: **Left:** EVB curves at different different asymmetries α_{as} . The initial state reorganization energy is $\Lambda_I = 40$ while the final state reorganization energy $\Lambda_F \in [20, 60]$. The reaction energy is $\Delta\Omega = 0$ for all curves. **Right:** EVB curves as a function of the reaction energy: $\Delta\Omega \in [-15, 15]$. For all curves $\Lambda_I = \Lambda_F$. **Both:** The dashed line at $x = 0$ indicates the position of the transition state when $\Lambda_I = \Lambda_F$ and $\Delta\Omega = 0$. The curve crossing point equals $\Delta\Omega_{dia}^\ddagger$

556 adiabaticity correction. For the canonical ensemble, this correction is known
 557 as the Hwang-Åqvist-Warshel equation[111]. If the GCE-diabatic states are
 558 quadratic along the reaction coordinate and share the same curvature along
 559 the reaction coordinate, the adiabatic barrier can be written as [111, 112]

$$\begin{aligned} \Delta\Omega_{ad,EVB}^\ddagger &= \frac{(\Delta\Omega + \Lambda)^2}{4\Lambda} - \Omega_{IF}(x^\ddagger) + \frac{(\Omega_{IF}(x^I))^2}{\Delta\Omega + \Lambda} \\ &= \Delta\Omega_{dia}^\ddagger - \Omega_{IF}(x^\ddagger) + \frac{(\Omega_{IF}(x^I))^2}{\Delta\Omega + \Lambda} \end{aligned} \quad (22)$$

560 where Ω_{IF} is the off-diagonal matrix of the GCE-EVB Hamiltonian in
 561 Eq. (14). If the Condon approximation is used, the above equation is greatly
 562 simplified as $\Omega_{IF} \approx \Omega_{IF}(x^\ddagger) \approx \Omega_{IF}(x^I)$. From a practical perspective it is
 563 interesting to observe how the adiabatic GCE-EVB barrier changes when the
 564 parameters are changed. From the schematics shown in Figures 3.1 and 3.2,
 565 one can observe that changes of the minima along the reaction coordinate

566 correspond to horizontal displacements of the diabatic states and and changes
 567 in Λ . Vertical changes correspond to changes in the reaction grand energy
 568 $\Delta\Omega$. Usually one concentrates only on changes in the free energy as reor-
 569 ganization coordinate not expected change for similar reactions or different
 570 electrode potentials (this assumptions is also made in Section 4.) Focusing on
 571 the reaction grand energy, it is easy show that under equilibrium conditions,
 572 $\Delta\Omega = 0$, the barrier is given by

$$\Delta\Omega_{ad,EVB}^{0,\ddagger} = \frac{\Lambda}{4} - \Omega_{IF} + \frac{(\Omega_{IF})^2}{\Lambda} \approx \frac{\Lambda}{4} - \Omega_{IF} \quad (23)$$

573 which leads to $\Lambda = 4(\Delta\Omega_{ad,EVB}^{0,\ddagger} + \Omega_{IF}) \approx 4\Delta\Omega_{dia}^{0,\ddagger}$ assuming that $\Omega_{IF} \ll$
 574 Λ . The equilibrium point is characterized by zero over-potential $\eta = \Delta\Omega = 0$.
 575 Replacing the solution for Λ in Eq. (22) gives the diabatic barrier as

$$\Delta\Omega_{dia}^{\ddagger} = \Omega_{dia}^{0,\ddagger} \left(1 + \frac{\Delta\Omega}{4\Omega_{dia}^{0,\ddagger}} \right)^2 = \Delta\Omega_{dia}^{0,\ddagger} + \frac{\Delta\Omega}{2} + \frac{(\Delta\Omega)^2}{16\Delta\Omega_{dia}^{0,\ddagger}} \quad (24)$$

576 Inserting (24) in (22) results in the adiabatic reaction barrier as

$$\Delta\Omega_{ad,EVB}^{\ddagger} = \Delta\Omega_{ad,EVB}^{0,\ddagger} + \frac{\Delta\Omega}{2} + \frac{(\Delta\Omega)^2}{16\Delta\Omega_{dia}^{0,\ddagger}} \quad (25)$$

577 This result has several interesting implications and connections to previ-
 578 ous work. The most immediate is that at small changes in the driving force
 579 $\Delta\Omega$, a linear dependence between the barrier and reaction energy is estab-
 580 lished. However, at larger driving forces, a non-linear dependence appears.

581 This can be directly translated to the language of electrochemistry by
 582 considering the changes in driving force as a function of the electrode poten-
 583 tial or over-potential. As discussed by Trasatti[113, 114] and in our recent
 584 work[3], the absolute electrochemical potential and chemical potential are
 585 related by $E^M(abs) = E^M(red) + K$ with $E^M(red) = \Delta\phi_S^M - \mu_n^M$ where
 586 $E^M(red)$ is the reduced absolute potential, K is used to convert between
 587 different reference choices, $\Delta\phi_S^M$ is the Galvani potential difference between
 588 the metal M and solution S , and μ_n^M is the chemical potential of the elec-
 589 trode. Independent of the reference scheme, the changes in the electrode
 590 potential are directly related to the changes in the electrochemical potential
 591 of the electrons: $E^M(abs) \sim -\tilde{\mu}_n$. It is important to notice that for micro-
 592 scopic systems usually considered within GCE-DFT keeping $\tilde{\mu}_n$ fixed leads

593 to changes in the number of electrons in the initial and final states. As a
 594 result the canonical free energies $A(N)$ do not remain constant when change
 595 when $\tilde{\mu}_n$ is changed. Therefore, changes in the grand energy is in general
 596 $\delta\Omega = A(N_F; \tilde{\mu}) - A(N_I; \tilde{\mu}) - \tilde{\mu}_n(N_I - N_F)$.

597 $\delta\Omega$ may be extracted from constant potential calculations enabling the
 598 study of electrochemical kinetics as a function of the electrode potential:
 599 $-\partial r(T, V, \tilde{\mu}_n)/\partial \tilde{\mu}_n$ as done in a Tafel analysis, for example. The traditional
 600 measure in electrochemistry for reaction kinetics is the Tafel slope measuring
 601 how current is affected by changes in the over-potential. In heterogeneous and
 602 homogeneous catalysis the corresponding quantity is the Brønsted-Evans-
 603 Polanyi (BEP) coefficient or more generally (linear free) energy relations
 604 measuring the change of reaction rate when the reaction energy is changed.
 605 However, the work of Fletcher[115, 116] and Parsons[117] show that Tafel and
 606 BEP type analyses actually measure the same quantities; both measure the
 607 reaction rate as a function of the changes in the reaction driving force. For
 608 macroscopic electrochemical reactions the driving force is measured in terms
 609 of the over-potential while in microscopic calculations the driving force is the
 610 free energy. These two quantities are linked by $|\Delta\eta| = |\Delta\tilde{\mu}_n| = |\Delta\partial\Omega/\partial n|$.

611 Both the BEP and Tafel coefficients maybe computed from a single ex-
 612 pression. The Tafel coefficient is defined as[2, 115, 116]

$$\alpha \propto \frac{\partial \ln k}{\partial E} = -\frac{\partial \ln k}{\partial \Delta\Omega} \frac{\partial \Delta\Omega}{\partial \tilde{\mu}_n} \frac{\partial \tilde{\mu}_n}{\partial E} = -\gamma \Delta\Omega' \quad (26)$$

613 where γ is BEP relationship and $\Delta\Omega'$ denotes the grand energy change
 614 as a function of the over-potential. Also $E \sim \tilde{\mu}_n$ has been used.

615 Let us focus first on the $\Delta\Omega'$ term which depends on the reaction and
 616 needs to be approximated. To facilitate this analysis, one recognizes that
 617 $\Delta\Omega = (A_F(\langle N_F \rangle) - A_I(\langle N_I \rangle) - \tilde{\mu}_n(\langle N_F \rangle - \langle N_I \rangle))$. For macroscopic systems,
 618 i) chemical reactions have $N_F = N_I$ while ii) simple electrochemical steps
 619 have $N_F = N_I \pm 1$. Then for chemical reactions $\Delta\Omega = \Delta A$ and the variation
 620 $\Delta\Omega'$ is expected to be small. For electrochemical reactions at the macro-
 621 scopic limit, a particularly straightforward estimate is obtained from the
 622 computational hydrogen electrode (CHE) concept.[118] In the CHE model,
 623 the reaction energy $\Delta\Omega \approx \Delta A^0 \mp \eta$ for PCET steps with ΔA^0 computed
 624 without any bias potential. Hence, within CHE, $\alpha = \gamma$ for PCET steps and
 625 zero otherwise. Similar reasoning holds also for simple (outer-sphere) ET re-
 626 actions in macroscopic systems as shown in Appendix E. For these reactions
 627 $\Delta\Omega \approx \Delta A^0 \mp \text{constant} \times \eta$ and $\Delta\Omega' = \mp \text{constant}$.

628 For microscopic systems, however, such a simple relationship does not
 629 hold in general and models such as GCE-DFT can be used for computing
 630 $\Delta\Omega'$ explicitly. Thus far, $\Delta\Omega'$ has been reported in only few studies[20,
 631 119]. In both works, $\Delta\Omega$ exhibits a roughly linear dependence on the applied
 632 potential. To conclude, $\Delta\Omega'$ is expected to be a constant close to unity for
 633 electrochemical reactions and close to zero for chemical reactions.

Next, the BEP γ of Eq (26) is analyzed. Using the diabatic barriers, one obtains

$$\begin{aligned} \gamma &= \left. \frac{\partial \ln k(T, V, \tilde{\mu}_n)}{\partial \Delta\Omega} \right|_{T,V} \\ &= \frac{\partial \ln \exp[-\beta\Omega^\ddagger]}{\partial \Delta\Omega} = \left[\frac{1}{2} + \frac{\Delta\Omega}{8\Delta\Omega_{dia}^{0,\ddagger}} \right] = \frac{1}{2} \left[1 + \frac{\Delta\Omega}{\Lambda} \right] \end{aligned} \quad (27)$$

634 From the above equation, it is seen that γ is not a simple constant but
 635 depends linearly on the reaction driving force. If the reorganization energy
 636 is small the dependence on the reaction grand energy becomes more pro-
 637 nounced. Based on the generalized BEP-Tafel energy identities the following
 638 relationships can be observed:

- 639 • If the quadratic part in Eq.(24) is neglected, one obtains the Butler-
 640 Volmer (BV) barrier. In this case the barrier depends linearly on
 641 the applied potential as $\Delta\Delta\Omega_{dia,EVB}^\ddagger \approx 0.5(A_F(\langle N_F \rangle) - A_I(\langle N_I \rangle) -$
 642 $\mu_{el}(\langle N_F \rangle - \langle N_I \rangle))$. μ_{el} is implicitly referenced against $\mu_{el}^{eq} = 0$ and can
 643 easily be converted to the over-potential $\mu_{el} - \mu_{el}^{eq} = \Delta\eta$. Note that
 644 $\Delta\Delta\Omega_{dia,EVB}^\ddagger$ is not expected to be linear for finite-sized systems.

645 Again, for macroscopic systems $\langle N_F \rangle = \langle N_I \rangle$ and $\Delta\Delta\Omega_{dia,EVB}^\ddagger = \Delta\Delta A_{dia,EVB}^\ddagger =$
 646 $0.5(A_F - A_I)$ which is the Brønsted-Evans-Polanyi result. The BV
 647 relationship is obtained by treating a specific reaction type. For ex-
 648 ample, in a typical ET, PT, or PCET the potential-dependent reac-
 649 tion free energy is given by $\Delta A = \Delta A(\eta = 0) \pm (n\eta)$. Using this for
 650 $\Delta\Delta A = \pm 0.5n\eta$.

- 651 • Non-linearity of the grand energy barrier was already established above.
 652 For macroscopic systems non-linearity is established by including the
 653 quadratic part of the diabatic barrier in model. Lately[20, 36, 38] this
 654 has been observed computationally and it is pleasing that the GCE-
 655 EVB picture seems qualitatively correct.

656 A spectacular feature of canonical Marcus and EVB theory is the observa-
657 tion of an inverted region *i.e.* the rate constant starts to decline as the reac-
658 tion becomes more exothermic. However, the inverted region has not been ob-
659 served for electrochemical reactions even at large over-potentials. The grand
660 canonical Marcus rate of Eq. (18) seems to predict an inverted region for
661 highly exothermic conditions. However, as written in the Tafel equation (26)
662 the rate as a function of the over-potential depends on both the change in A)
663 barrier as a function of the reaction energy and B) change reaction energy as a
664 function of the over-potential. A) would indeed predict an inverted region but
665 B) suppress this if $\Delta\Omega \approx 0$. Then the Tafel slope would approach zero as pre-
666 dicted by the Marcus-Hush-Chidsey[120], Dogonadze-Levich-Kuznetsov[49,
667 50], Newns-Anderson-Schmickler, Soudackov-Hammes-Schiffer[45] models of
668 ET and PCET [51] (see also Appendix A). At the moment, there is not
669 enough computational nor theoretical evidence on the behaviour of $\Delta\Omega$ as
670 a function of the over-potential to predict or to analyze the Tafel slope any
671 further.

672 To summarize, the generalized BEP-Tafel relationships has been derived
673 from a microscopic perspective starting from a grand canonical rate theory.
674 Both variation in the reaction energy barrier and the transition state location
675 as a function of the potential can be predicted using just a few parameters.
676 The general form of the BEP-Tafel relation is given in Eq. (26). For small
677 over-potentials, the rate is expected to depend linearly on the applied poten-
678 tial. For larger over-potentials non-linear dependence is predicted, especially
679 reactions for which the reorganization energy is small.

680 4. Non-adiabatic ET and PCET reaction rates within GCE

681 4.1. Non-adiabatic ET rate

682 As shown above, computation of adiabatic reaction rates from either
683 GCE-HTST, GCE-EVB or GCE-perturbation theory do not yield any fun-
684 damental difficulties as compared to the canonical case; after finding the
685 barrier, one can simply use a simple TST-like expression to compute the re-
686 action rate using grand free energies. However, for a non-adiabatic process,
687 using the grand free energy is not as straightforward. The main difficulty
688 becomes from computation of the electronic transition matrix element which
689 is not defined for states with different number of electrons. Hence, one can-
690 not directly use the effective GCE-EVB states developed in Section 3 and

691 use them to compute the non-adiabatic rate. Instead, the electronic tran-
 692 sition matrix element needs to be computed separately for each canonical
 693 transition. Afterwards, a summation over the canonical rates is performed
 694 to express the non-adiabatic ET/PCET rate as a expectation value. To ob-
 695 tain the non-adiabatic TST rate, the Golden-rule approach is used herein. In
 696 the canonical ensemble, the Golden-rule formulation of the rate is equivalent
 697 to Dogonadze’s treatment.[49, 50, 101] Below theory for the computation of
 698 non-adiabatic ET and PCET rates within GCE is developed.

699 To start with, the electronic states $|iN\rangle$ are specified and they are eigen-
 700 states to the electronic Hamiltonian \hat{H}_N^{el} . Electronic states are defined for
 701 initial (i) and final (f) states with a fixed number of particles (N). Then the
 702 electronic energies for the initial and final states at fixed particle number at
 703 nuclear geometry Q are

$$\langle iN|\hat{H}_N^{el}|iN\rangle = \varepsilon_{iN}(Q) \quad \text{and} \quad \langle fN|\hat{H}_N^{el}|fN\rangle = \varepsilon_{fN}(Q) \quad (28)$$

704 Within the Born-Oppenheimer approximation (BOA), the nuclear wave
 705 functions and their energies ϵ in the initial ($|mN\rangle$) and final ($|nN\rangle$) electronic
 706 states are obtained from

$$\begin{aligned} [\hat{T}_Q + \varepsilon_{iN}(Q)] |mN\rangle &= \epsilon_{mN} |mN\rangle \quad \text{and} \\ [\hat{T}_Q + \varepsilon_{fN}(Q)] |nN\rangle &= \epsilon_{nN} |nN\rangle \end{aligned} \quad (29)$$

707 where \hat{T}_Q is the nuclear kinetic energy. Within BOA, the total vibronic
 708 wave function and the corresponding energy factorize as

$$|imN\rangle = |iN\rangle |mN\rangle \quad \text{and} \quad E_{imN} = \varepsilon_{iN} + \epsilon_{mN} \quad (30a)$$

$$|fnN\rangle = |fN\rangle |nN\rangle \quad \text{and} \quad E_{fnN} = \varepsilon_{fN} + \epsilon_{nN} \quad (30b)$$

709 As the different energy contributions are additive, the canonical partition
 710 functions can be factorized:

$$\begin{aligned} Q_i^N &= \exp[-\beta\varepsilon_{iN}] \sum_m \exp[-\beta\epsilon_{mN}] \quad \text{and} \\ Q_f^N &= \exp[-\beta\varepsilon_{fN}] \sum_n \exp[-\beta\epsilon_{nN}] \end{aligned} \quad (31)$$

711 At this point all relevant canonical quantities have been defined and the
 712 focus turns to the GCE formulation of the Golden-rule rate. The GCE
 713 partition function for the initial state is

$$\Xi_i = \sum_N \exp[\beta\mu N] Q_i^N \quad (32)$$

714 This equation is inserted in the general GCE rate expression. For the non-
 715 adiabatic limit, the Golden rule rate is used. As shown in Appendix C and
 716 Appendix A, use of the Golden rule expression is consistent with the general
 717 rate theory based on the flux approach if the non-adiabatic Hamiltonian and
 718 suitable flux operator are utilized. The GCE-NATST rate constant is then

$$\begin{aligned} k_{GCE-NATST} &= \frac{2\pi}{\hbar \Xi_i} \sum_N e^{-\beta(\varepsilon_{iN} - \mu N)} \sum_{m,n} e^{-\beta\epsilon_{mN}} \left| \langle N n f | \hat{V}_N | i m N \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \\ &= \frac{2\pi}{\hbar} \sum_N \sum_{m,n} p_{imN} \left| \langle N n f | \hat{V}_N | i m N \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \end{aligned} \quad (33)$$

719 where p_{imN} is the population of the vibronic state $|imN\rangle$. Next, a
 720 significant simplification is made; it is assumed that the vibrational part
 721 of the canonical function does not depend on the number of electrons in
 722 the systems. This assumption gives $Q_i^N = \exp[-\beta\varepsilon_{iN}] \sum_m \exp[-\beta\epsilon_{mN}] \approx$
 723 $\exp[-\beta\varepsilon_{iN}] \sum_m \exp[-\beta\epsilon_m] = \exp[-\beta\varepsilon_{iN}] Q_m$ and the GCE partition func-
 724 tion becomes

$$\Xi_i \approx Q_m \sum_N \exp[-\beta(\varepsilon_{iN} - \mu N)] = Q_m \Xi_i \quad (34)$$

725 Inserting this approximation in the GCE-NATST rate expression gives

$$\begin{aligned} k_{GCE-NATST} &\approx \frac{2\pi}{\hbar \Xi_i} \sum_N e^{-\beta(\varepsilon_{iN} - \mu N)} \sum_{m,n} \frac{e^{-\beta\epsilon_{mN}}}{Q_m} \left| \langle N n f | \hat{V}_N | i m N \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \\ &= \frac{2\pi}{\hbar} \sum_N p_{iN} \sum_{m,n} p_{mN} \left| \langle N n f | \hat{V} | i m N \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \end{aligned} \quad (35)$$

726 where $p_{iN,el} = \exp[-\beta(\varepsilon_{iN} - \mu N)] / \Xi_{i,el}$ and $p_{mN} = \exp[-\beta\epsilon_{mN}] / Q_m$.

727 This equation has the structure of the canonical Golden rule rate weighted
728 by the probability of being in the initial electronic state iN . To simplify the
729 notation, one can momentarily concentrate only on the canonical part of the
730 above rate expression. Using the Fourier transform presentation of the delta
731 function, gives

$$\begin{aligned}
& \sum_{m,n} p_{imN} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \\
&= \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \int dt e^{it(E_{imN} - E_{fnN})/\hbar} \\
&= \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \langle fmN | \hat{V}_N | inN \rangle \langle inN | \hat{V}_N | fmN \rangle \int dt e^{it(E_{imN} - E_{fnN})/\hbar} \\
&\approx \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \left| \langle fN | \hat{V}_N | iN \rangle \right|^2 \int dt \langle mN | nN \rangle \langle nN | mN \rangle e^{it(E_{imN} - E_{fnN})/\hbar} \\
&= \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} V_{N,if}^2 \int dt \left| \langle nN | mN \rangle_q \right|^2 e^{it(E_{imN} - E_{fnN})/\hbar} \\
&= \frac{V_{N,if}^2}{2\pi\hbar} \int dt \langle e^{it(E_{imN}/\hbar} e^{-it(E_{fnN})/\hbar} \rangle_q = \frac{V_{N,if}^2}{2\pi\hbar} \int dt C(t)
\end{aligned} \tag{36}$$

732 where $C(t)$ is an energy autocorrelation function. The last two equations
733 are amenable to two different ways of computing the rate constant. The last
734 can be used with a cumulant expansion approach, while the second last has
735 the form of a thermally averaged Franck-Condon treatment. The cumulant
736 expansion is presented in the main text while the Franck-Condon treatment
737 is presented in Appendix G for completeness.

738 In the present work, nuclear degrees of freedom are treated classically.
739 Following either Geva[121] or Marcus[122], the autocorrelation function can
740 be expressed using a cumulant expansion[123]. Using the second order cu-
741 mulant expansion results in

$$\begin{aligned}
& \langle \exp[iE_{fnN}t/\hbar] \exp[iE_{imN}t/\hbar] \rangle_i \approx \\
& \exp \left[\frac{-it}{\hbar} \langle \Delta E_{fi}^N \rangle - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C(\tau_1 - \tau_2) \right]
\end{aligned} \tag{37}$$

742 where $\langle \Delta E_{fi}^N \rangle$ is the average free energy gap between the final and ini-
 743 tial electronic diabatic states. Also $C(\tau_1 - \tau_2) = \langle \delta \Delta E_{fi}^N(\tau) \delta \Delta E_{fi}^N(0) \rangle$ where
 744 $\delta \Delta E_{fi}^N = \Delta E_{fi}^N - \langle \Delta E_{fi}^N \rangle$. $C(\tau_1 - \tau_2)$ is directly linked to the vibrational spec-
 745 tral density of the system[55, 101, 122, 124]. To obtain a manageable expres-
 746 sion for the rate, the short time approximation or slow fluctuation limit[125]
 747 to the correlation function is used: $C(\tau_1 - \tau_2) \approx C(0) = \langle \delta(\Delta E_{fi}^N)^2 \rangle$. Insert-
 748 ing this in Eq. (37) yields

$$\exp \left[-\frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C(\tau_1 - \tau_2) \right] \approx \exp \left[-\frac{t^2}{\hbar^2} \langle \delta(\Delta E_{fi}^N)^2 \rangle \right] \quad (38)$$

749 This is inserted in Eq. (36) to give

$$\begin{aligned} & \sum_{m,n} p_{imN} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \\ & \approx \frac{V_{N,if}^2}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp \left[\frac{it}{\hbar} \langle \Delta E_{fi}^N \rangle - \frac{t^2}{\hbar^2} \langle \delta(\Delta E_{fi}^N)^2 \rangle \right] \\ & = \frac{V_{N,if}^2}{2\pi\hbar} \sqrt{\frac{2\pi\hbar^2}{\langle \delta(\Delta E_{fi}^N)^2 \rangle}} \exp \left[\frac{-\langle \Delta E_{fi}^N \rangle^2}{2\langle \delta(\Delta E_{fi}^N)^2 \rangle} \right] \\ & \approx \frac{V_{N,if}^2}{2\pi} \sqrt{\frac{\pi}{k_B T \lambda}} \exp \left[-\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} \right] \end{aligned} \quad (39)$$

750 where on the last line it has been assumed that the free energy surfaces are
 751 quadratic along the energy gap coordinate. The reorganization and reaction
 752 energies are defined as $\lambda = E_{im}(Q_F) - E_{fn}(Q_F)$ and $E_{fi}^N = E_{fn}^N(Q_F) -$
 753 $E_{im}^N(Q_I)$ (see Fig. 3.1). A generalization to asymmetric GCE-diabatic energy
 754 curves can be made following Mattiat and Richardson[74]. Furthermore, it
 755 is assumed that the curvature of the quadratic surfaces is the same for all
 756 particle numbers N in which case the reorganization energy does not depend
 757 on N . This should be to a rather good approximation as the reorganization
 758 is related to the reorientation of the surrounding medium which is expected
 759 be rather insensitive to the number of electrons in the system. For example,
 760 in the spin-boson model, which in the canonical ensemble yields the Marcus
 761 rate, the reorganization energy is only related to the bath frequencies in
 762 thermal equilibrium.[101] If the spin-boson model is applied to the present

763 GCE case, the vibrational, bosonic Hamiltonian would be assumed to be
 764 independent of the number of electrons and yield directly the reorganization
 765 energy which is independent of the number of particle for the GCE. The
 766 assumption that the reorganization energy is independent on the particle
 767 number can also be reinforced by doing a re-derivation of the rate using the
 768 thermalized Franck-Condon approach as shown in the Appendix G.

769 Finally, the final GCE-NATST result is obtained by combining Eq. (35)
 770 with either Eq. (37) or (G.2) to give

$$k_{GCE-NATST}^{Marcus} = \sum_N p_{iN} \frac{V_{N,if}^2}{\hbar\sqrt{4\pi k_B T \lambda}} \exp \left[-\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} \right] \quad (40)$$

771 The reorganization energy can also be separated to inner and outer sphere
 772 components as discussed in Section Appendix H. If this separation is invoked,
 773 one can alleviate the assumption that the total reorganization is independent
 774 of the particle number and instead assume that only bulk solvent (outer
 775 sphere) reorganization is a constant while the inner-sphere reorganization
 776 energy depends on the particle number.

777 4.2. PCET kinetics within GCE

778 The PCET kinetics is based on the PCET rate theory of Soudackov and
 779 Hammes-Schiffer. Within the canonical ensemble the relevant rate expres-
 780 sions were derived in Refs. 45, 53–55 and here this treatment is extended
 781 to the GCE yielding PCET rate constants at fixed electrode potentials. The
 782 PCET rate constant derivation follows a similar procedure as the one used
 783 above for the ET rates. In the case of PCET, an additional geometric vari-
 784 able q to denote the position of the transferring proton is introduced. Within
 785 BOA, the total vibronic wave function is then

$$|iumN\rangle = |iN(q, Q)\rangle |uN(Q)\rangle |mN\rangle \quad (41)$$

786 where it is explicitly written that the electronic wave function $|iN\rangle$ de-
 787 pends explicitly on the proton q and system coordinate Q while the proton
 788 wave function $|uN(Q)\rangle$ depends on the system coordinate Q . The wave func-
 789 tions and corresponding energies are solved using equations similar to the ET
 790 case

$$\begin{aligned} \langle iN | \hat{H}_N^{el} | iN \rangle &= \varepsilon_{iN}(q, Q) \quad \text{and} \\ \langle fN | \hat{H}_N^{el} | fN \rangle &= \varepsilon_{fN}(q, Q) \end{aligned} \quad (42a)$$

$$\begin{aligned}
[\hat{T}_q + \varepsilon_{iN}(q, Q)] |iuN\rangle &= \epsilon_{uN}^i |iuN\rangle \quad \text{and} \\
[\hat{T}_q + \varepsilon_{fN}(q, Q)] |fvN\rangle &= \epsilon_{vN}^i |fvN\rangle
\end{aligned} \tag{42b}$$

$$\begin{aligned}
[\hat{T}_Q + \epsilon_{uN}^i] |mN\rangle &= \mathcal{E}_{mN} |mN\rangle \quad \text{and} \\
[\hat{T}_Q + \epsilon_{vN}^f] |nN\rangle &= \mathcal{E}_{nN} |nN\rangle
\end{aligned} \tag{42c}$$

791 where \hat{T}_q and \hat{T}_Q are the kinetic energy operators for the proton and
792 other nuclei, respectively. Within BOA, the total energy of the at fixed N is
793 written as a simple sum of the three contributions:

$$E_{iumN} = \varepsilon_{iN} + \epsilon_{uN}^i + \mathcal{E}_{mN} \tag{43}$$

794 and similarly for the final diabatic state.

795 The SHS treatment of PCET rates is valid for reactions ranging from
796 vibronically non-adiabatic to vibronically adiabatic scenarios[126] and rate
797 expressions for various well-defined limits have been achieved. The SHS
798 PCET rate theories are derived following a path analogous to the derivation
799 of ET rates and extension to the GCE is rather straightforward. As done by
800 SHS, the Golden rule formulation is used. Then, the PCET rate constant is
801 written as

$$\begin{aligned}
k_{GCE-PCET} &= \frac{2\pi}{\hbar \Xi_i} \sum_{N,u,v,m,n} e^{-\beta(E_{iumN} - \mu N)} \left| \langle Nnvf | \hat{V}_N | iumN \rangle \right|^2 \delta(E_{iumN} - E_{fvnN}) \\
&= \frac{2\pi}{\hbar} \sum_N \sum_{u,v} \sum_{m,n} p_{iumN} \left| \langle Nnvf | \hat{V}_N | iumN \rangle \right|^2 \delta(E_{iumN} - E_{fvnN})
\end{aligned} \tag{44}$$

802 The obtained form is analogous to the GCE-ET theory developed herein
803 and shares the structure of the canonical PCET rate of SHS. As assumed
804 for ET part, it is expected that the vibrational part of the system does not
805 depend on the number of particles. However, no such assumption is made
806 for the transferring proton *i.e.* the proton potential depends on the charge
807 state. This is written as

$$\Xi_i = \sum_{N,u,m} e^{-\beta(E_{iumN} - \mu N)} \approx Q_m \sum_{N,u} e^{-\beta(\varepsilon_{iN} + \epsilon_{iuN} - \mu N)} = Q_m \Xi_{iu} \tag{45}$$

808 At this point it is important to stress that the vibronic coupling depends
 809 sensitively on the proton donor-acceptor distance R which is included in the
 810 rate expression. It is assumed that the coupling can be decomposed as

$$\langle Nnvf|\hat{V}(R)_N|iunN\rangle \approx \langle Nvf|\hat{V}(R)_N|iunN\rangle_q \langle Nn|mN\rangle_Q = V(R)_{uv}^N S_{nm}^N \quad (46)$$

811 Inserting these two approximations result in PCET rate constant of the
 812 form

$$\begin{aligned} k_{GCE-PCET} &\approx \frac{2\pi}{\hbar} \sum_{N,u,v} \frac{e^{-\beta(\epsilon_{iN} + \epsilon_{iuN} - \mu N)}}{\Xi_{iu}} \sum_{m,n} \frac{e^{-\beta \mathcal{E}_{mN}}}{Q_m} |V(R)_{uv}^N|^2 |S_{mn}^N|^2 \delta(E_{iunN} - E_{fvnN}) \\ &= \frac{2\pi}{\hbar} \sum_{N,u,v} p_{iuN} \sum_{m,n} p_m |V(R)_{uv}^N|^2 |S_{mn}^N|^2 \delta(E_{iunN} - E_{fvnN}) \end{aligned} \quad (47)$$

813 This form is amenable to the direct treatment as performed by SHS. De-
 814 pending on the treatment of the R coordinate, several appropriate limits may
 815 be considered each yielding a different canonical rate constant. The deriva-
 816 tions for the R -dependent PCET rates follow a similar (but more complex
 817 [55]) cumulant expansion as performed above for ET. Hence, the GCE-PCET
 818 rate can be obtained by extending the approach presented above for the ET.
 819 The extension of PCET in GCE is straight-forward and here I present only
 820 the most simple result valid under the same conditions as the Marcus-like
 821 expression derived above for ET. Specifically, one assumes that[127] i) the
 822 short time approximation of the energy gap correlation is valid, ii) high-
 823 temperature limit is taken, and iii) that the R coordinate is static giving

$$k = \sum_{N,u} p_{iu} \sum_v \frac{|V(R)_{uv}^N|^2}{\hbar \sqrt{4\pi k_B T \lambda_{uv}}} \exp \left[-\frac{(\Delta E_{uv}^N + \lambda_{uv})^2}{4k_B T \lambda_{uv}} \right] \quad (48)$$

824 where the reaction energy between vibrational states iuN and fvN is
 825 $E_{uv}^N = E_{fvnN}(q_F, Q_F) - E_{iunN}(q_I, Q_I)$. The state-dependent reorganization
 826 energy $\lambda_{uv} = E_{iunN}(q_F, Q_F) - E_{fvnN}(q_F, Q_F)$ is assumed independent of the
 827 particle number. If some vibrational modes (besides the R mode) are sen-
 828 sitive to changes in the particle number, they can be separated from the
 829 total reorganization energy by decomposing the total reorganization energy

830 to inner- and outer-sphere components as shown in Appendix H. Depending
831 on the form of the prefactor, both electronically and vibronically adiabatic
832 and non-adiabatic limits of PCET can be reached within the semiclassical
833 treatment[22, 128, 129] of the prefactor.

834 *4.3. Analysis of the non-adiabatic GCE rates*

835 The main difficulty observed in the GCE non-adiabatic rate theory is the
836 treatment of the electronic/vibronic coupling constant; this term is defined
837 only for particle conserving transitions. This precludes the straightforward
838 use of GCE diabatic states which have different number of electrons at the
839 same geometry. Only at the thermodynamic limit when the particle number
840 fluctuation is zero can the GCE diabatic states be used for computing the
841 coupling constant. However, at this limit the GCE-NATST is equal to the
842 canonical NATST as only a single particle number state is populated i.e.
843 p_i becomes a delta function around some particle number. At thermody-
844 namic limit either using fixed potential GCE states or fixed particle number
845 canonical states will give equivalent results as they should.

846 Even at the thermodynamic limit the present treatment differs from the
847 traditional Dogonadze-Kutzetnotsov-Levich[50]. Schmikler-Newns-Anderson[51,
848 52], and SHS approaches. A detailed discussion is given in the Appendix A
849 and here only the main differences are high-lighted. The crucial difference is
850 that the present formulation does not rely on the separation of the total inter-
851 acting wave function to non-interacting or weakly interacting fragments. In
852 the present approach, the applied electrode potential does not only affect the
853 electrode alone but rather modifies the entire systems affecting all electrode,
854 reagent, and solvent species. Hence, the inherent complexity of the elec-
855 trochemical interface is naturally included in the Hamiltonian and the wave
856 function from the start. Another crucial difference is that the charge trans-
857 fer kinetics are not decomposed into single electron orbital contributions.
858 Instead, the work herein formulates the kinetics in terms of many-body dia-
859 batic wave functions. In the canonical ensemble, such an approach has been
860 shown[130] to provide accurate barriers, prefactors, and overall kinetics for
861 electron transfer reaction in battery materials.

862 For small systems where particle number fluctuations are pronounced the
863 summation over particle numbers need to be performed. While straightfor-
864 ward in principle, the amount of calculations can seem daunting at first.
865 However, as the populations depend exponentially on the energy and tar-
866 get chemical potential, $p_{iN} \sim \exp[-\beta(E_{iN} - \mu N)]$, only a limited number of

867 states will contribute to the summation. In the Appendix F, it is shown that
868 for graphene, the electrode potential around the $PZC \pm 0.5V$ is accurately
869 captured using seven different charge states. It is expected that the infinite
870 summation can be safely reduced to summation over a small number (5–10)
871 of different charge states covering the electrode potential range of interest.
872 Again, at the thermodynamic limit only a single calculation *per* potential is
873 needed.

874 For practical applications interpolation between adiabatic and non-adiabatic
875 regions is often needed. The most commonly utilized way to achieve this in
876 the canonical ensemble is to use the Landau-Zener interpolation formula (see
877 *e.g.* Ref. 100). A similar interpolation can be performed also within the GCE
878 in two ways – for the fixed number states or the effective fixed potential.
879 In the former, the Landau-Zener prefactor is computed for each charge state
880 and utilized in the summation. In the latter one replaces the particle number
881 dependent prefactor with an effective or averaged prefactor as in Eqs.(7) or
882 (C.6). At the thermodynamic limit both will be equivalent. Investigating
883 this interpolation for smaller systems is not within the scope of the present
884 work and is left for future studies.

885 5. Conclusions

886 This work presents a general rate theory for open systems. If only the
887 electronic subsystem is open, the formulation yields electrochemical and elec-
888 trocatalytic rates at fixed electrode potentials. The rate equations are derived
889 by extending the canonical rate theory[61–63] to the grand canonical, fixed
890 potential ensemble. It is shown that all rate theories developed within the
891 canonical ensemble can be extended to GCE. Specifically, ways to address
892 *e.g.* adiabatic, non-adiabatic, and tunnelling reactions can be formulated
893 within GCE. In this work, the grand canonical formulation is applied to de-
894 rive rate constants for i) general electrocatalytic reactions with (Eq. (8))
895 and without (Eq. (2)) the TST approximation, ii) adiabatic ET and PCET
896 reactions using a grand canonical Marcus-like EVB theory in Eq. (18) , and
897 iii) non-adiabatic ET in Eq. (40) and PCET in Eq. (48). Future work will
898 provide interpolation between the derived adiabatic and non-adiabatic rate
899 equations. To summarize, the theoretical work presented herein provides a
900 unified framework for computing and understanding both inner-sphere (elec-
901 trocatalytic) and outer-sphere (electrochemical) reaction kinetics as a func-
902 tion of the electrode potential.

903 In its most general form, the fixed potential rate theory requires com-
904 putation of canonical rates for a set of systems with a varying number of
905 electrons (and/or nuclei). Summing and weighting the different canonical
906 ensemble rates can be relaxed if one assumes that the prefactor or trans-
907 mission coefficient is independent on the number of particles in the system.
908 Assuming a constant transmission coefficient directly leads to TST like equa-
909 tions (Eqs. (7) and (8)) where the reaction rate depends exponentially on
910 the grand energy barrier $\Delta\Omega^\ddagger$. This is most useful and provides the theoret-
911 ical basis for computing adiabatic reaction rates within GCE-TST as done
912 in several recent publications[12, 19, 20, 35, 36, 131, 132] in which the rate
913 expression was used without *a priori* justifying the use of such rate equations.

914 Further insight in the (adiabatic) reaction rates and energy barriers is
915 obtained from a Marcus-like, grand canonical ensemble empirical valence
916 bond (GCE-EVB) theory developed in the present work. As shown in Section
917 3, the GCE-EVB formulation enables writing the grand energy barrier in
918 terms of fixed potential reorganization energy and the reaction grand energy
919 in analogy with the canonical EVB or Marcus theory. As discussed in Section
920 3.2, this formulation enables computation and rationalization of both non-
921 linear grand energy relationships and Tafel slopes. Together these may called
922 BEP-Tafel relations. Both can be derived, analyzed and computed using
923 just a few parameters which can be obtained using *e.g.* a combination of
924 fixed potential and constrained DFTs. Based on the BEP-Tafel relationships
925 one determine how the reaction barrier changes as a function of the reaction
926 energy as shown in Figure 3.2. The derived adiabatic GCE-EVB rate, barrier
927 and generalized BEP-Tafel energy relation predict and explain the "Marcus-
928 like" behavior in energy barriers as a function of the thermodynamic driving
929 force observed in recent computational work[20, 36, 38].

930 To go beyond TST, fixed potential rate constants are derived also for elec-
931 tronically (and vibronically) non-adiabatic ET and PCET reactions. Thus
932 far computational work on non-adiabatic effects and pure ET have remained
933 scarce despite their practical importance in providing new reaction pathways
934 to avoid constraining scaling relations[133–135] encountered for adiabatic
935 PCET reactions while predicting catalytic activity as well as in understand-
936 ing fundamental phenomena in electrocatalysis. As discussed by Schmickler
937 *et.al* in Ref. [136], the absence of computational studies on pure ET in
938 electrocatalytic systems is due to insufficient theoretical and computational
939 methods. The NA-ET rate constants derived herein will especially useful for
940 studying NA effects in outer-sphere ET of electrocatalytic systems. This pro-

941 vides means to obtain atomic-level insight on pure ET reactions which have
942 remained elusive and neglected in computational studies but have often been
943 observed experimentally, especially on weakly-binding catalysts, as discussed
944 in Section 1. The fixed potential PCET rate equations facilitate the study
945 of kinetics of ubiquitous proton-coupled electron transfer reactions. As for-
946 mulated herein, the PCET rate constant naturally includes both electronic
947 and vibronic non-adiabaticity as well as hydrogen tunneling. This again en-
948 ables detailed theoretical and computational studies of these experimentally
949 observed, but thus far computationally largely neglected, electrocatalytic re-
950 actions.

951 All the rate equations derived in this work can be directly utilized and
952 combined with general Hamiltonians used in *e.g.* electronic DFT. For non-
953 adiabatic kinetics and GCE-EVB, methodology for computing diabatic curves
954 is needed; constrained DFT[95–97] implemented in various DFT codes[137–
955 147] is ideally suited for this and facilitates adopting the rate equations de-
956 rived herein. TST-like rate equations can be computed using energies from
957 grand canonical DFT which is also currently available in several codes in
958 various forms[3, 10–20].

959 Combining the presented rate theory with currently existing DFT meth-
960 ods and various solvation models is straight-forward and enables the study
961 of electrochemical and electrocatalytic kinetics at realistic electrochemical
962 interfaces. This will greatly improve our microscopic understanding by en-
963 abling computation of electrocatalytic kinetics as a function of the electrode
964 potential and addressing tunneling and non-adiabaticity in electrocatalysis.
965 Hence, a wide variety of mechanistic, kinetic and thermodynamic aspects of
966 electrocatalytic reactions can be addressed on equal footing within GCE and
967 the complex interplay between the electrode potential, solvation, double-layer
968 and electrocatalysis can be studied from first principles. Besides providing
969 a rigorous and general theoretical framework for fixed potential kinetics, the
970 advances herein enable computational studies on pure ET and PCET with
971 hydrogen tunnelling pathways to circumvent scaling relations often encoun-
972 tered in electrocatalysis.

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981 7. Declaration of interest

982 Declarations of interest: none

983 Appendix A. Problem for choosing filled and empty orbitals in 984 "orbital-based" rate theories

985 *Appendix A.1. Orbital based electron transfer rate theories*

986 There are two commonly used orbital based approaches for writing the
987 charge transfer rate at an electrode surface. The first one was developed
988 by Dogonadze, Levich, and Kuznetsov (DLK)[49], who assumed a weak
989 interaction between the donor and acceptor. Their treatment yields an ex-
990 pression similar to Marcus theory and the model is often called Marcus-Hush-
991 Chidsey[120], Gerischer[148], Marcus-DOS[148] or just the density-of-states
992 (DOS) model. In the case of a metallic electrode, the molecular orbital will
993 interact with a continuum of electronic states from the metal and therefore
994 one needs to integrate over all the metallic bands. An implicit assumption in
995 the DOS model is that charge transfer takes place between two one-electron
996 orbitals rather than two many-electron wave functions. Also, the effect of
997 the electrode potential E is assumed to linearly shift the energy of the initial
998 state without changing the one-electron levels. For electrochemical charge
999 transfer reactions the DOS equation written in terms of a molecular orbital
1000 ϵ_0 and its DOS $\rho_0(\epsilon_0)$ and (quasi-continuum) of electrode bands ϵ with DOS
1001 $\rho(\epsilon)$. In this case the charge transfer is [49, 50] (see also Appendix A)

$$k_{DOS}(E) = \int d\epsilon W(\epsilon, \epsilon_0) f(\epsilon - E) \rho(\epsilon) \rho_0(\epsilon_0) \quad (\text{A.1})$$

1002 where W is the transition probability and f is the Fermi-Dirac distribu-
1003 tion. Originally, the DLK model was derived for the weak interaction limit
1004 and harmonic energy surfaces results in the well-known equation [49, 50]

$$k_{DOS}(E) \approx \sqrt{\frac{\beta}{4\pi\lambda}} \int_{-\infty}^{\infty} d\epsilon |H_{ab}(\epsilon, \epsilon_0)|^2 f(\epsilon - E) \exp\left[-\beta \frac{(\lambda + e_0(E^0 - E) - \epsilon_0)^2}{4\lambda}\right] \quad (\text{A.2})$$

1005 $H_{ab}(\epsilon, \epsilon_0) = \langle \psi_a^{\epsilon_0} | \hat{H} | \psi_b^\epsilon \rangle$ denoting the Hamiltonian matrix element be-
 1006 tween the molecule and electrode orbitals corresponding to energy levels ϵ_0
 1007 and ϵ , respectively, in the initial a and final b diabatic states. E is the elec-
 1008 trode potential and E^0 is the formal equilibrium potential. Depending on the
 1009 model used for the reactant DOS, the weakly interacting limit by Dogonadze,
 1010 Gerischer's model with a Gaussian dependency or Schmickler's model (see
 1011 below) maybe obtained as shown in Ref. 149

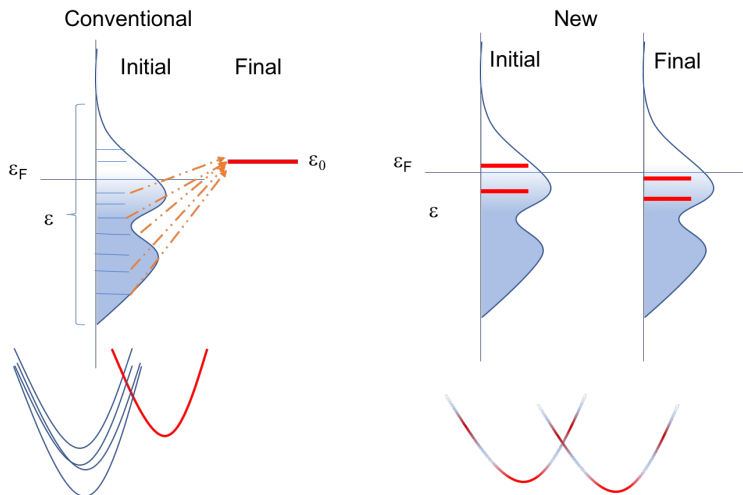


Figure A.4: Conventional (left) and GCE Marcus theory (right). The conventional theory is based on transitions between single-electron orbitals while the current GCE framework utilized general many-electron wave functions.

1012 The other approach is due to Schmickler[51, 52] and has been dubbed
 1013 as the potential energy curve (PEC) method. The PEC method applies a
 1014 modified Newns-Anderson (N-A) Hamiltonian for building potential energy
 1015 surface (pes)

$$\begin{aligned}
H_{N-A} = & \epsilon_0 n_0 + \sum_k \epsilon_k n_k + \sum_k (v_{k0} c_k^\dagger c_r + v_{rk} c_0^\dagger c_k) \\
& + \frac{1}{2} \sum_i \hbar \omega_i (p_i^2 + q_i^2) + (n_0 - z) \sum_i (\hbar \omega_i g_i q_i)
\end{aligned} \tag{A.3}$$

1016 where the terms describe reactant orbital, orbitals of the electrode, elec-
1017 tron exchange terms using coupling matrix elements v , harmonic bath at
1018 frequencies ω_i , momenta p_i and coordinate q_i while the last term couples the
1019 reactant at charge state z to the harmonic bath. Connecting the initial and
1020 final states of the redox reaction along a charge transfer coordinate r_q and
1021 using N-A Hamiltonian, the PES is

$$\begin{aligned}
u(r_q, \epsilon_F) = & \frac{r_q^2}{4\lambda} + (\epsilon_0 + r_q - \epsilon_F) \langle n(r_q) \rangle \\
& + \frac{\Delta}{2\pi} \ln[(\epsilon_F - r_q - \epsilon_0) + \Delta^2]
\end{aligned} \tag{A.4}$$

1022 where $\langle n(r_q) \rangle = 1/2 + 1/\pi \tan^{-1}((\epsilon_F - r_q - \epsilon_0)/\Delta)$ is the charge at r_q and
1023 $\Delta(\epsilon') = \pi \sum_k |v_{0,k}|^2 \delta(\epsilon' - \epsilon_k)$ is the effective coupling constant. Then, the
1024 charge transfer barrier is $u^\ddagger = u(r_q = r_{max}, \epsilon_F) - u(r_q = 0, \epsilon_F)$ and the rate
1025 is

$$k_{PEC} = \kappa \exp[-\beta u^\ddagger] \tag{A.5}$$

1026 At the weak interaction limit, both the DOS and PEC models are in
1027 their essence formulations of Fermi's Golden rule describing electron transfer
1028 between single electron orbitals.

1029 *Appendix A.2. Orbital based Fermi Golden rule formulation*

1030 If initial (final) state at the initial (final) geometry can be approximated
1031 by a single diabatic electronic state $\Psi(R_{initial}) \approx |\psi_I\rangle |\chi_j\rangle$, the Hamiltonian
1032 in Eq.(A.6) leading to Fermi's golden rule as follows. A similar equation can
1033 also be written for adiabatic states as shown in Ref. 93, 94. In the diabatic
1034 Fermi Golden rule formulation the Hamiltonian is [62, 72]

$$\begin{aligned}
\hat{H}_{el} &= \sum_i E_i^I |I^i\rangle \langle I^i| + \sum_f E_f^F |F^f\rangle \langle F^f| \\
&+ \sum_{if} \Delta_{if} (|I^i\rangle \langle F^f| + |F^f\rangle \langle I^i|)
\end{aligned} \tag{A.6}$$

1035 where $|K^k\rangle = |\psi_k\rangle |\chi_k\rangle$ is a vibronic wave function consisting of $|\psi_k\rangle$,
1036 a one electron orbital and $|\chi_k\rangle$ a nuclear wave function. Reaction rates
1037 using this diabatic Hamiltonian is achieved using the general flux formula-
1038 tion presented in the main article with the following transition proba-
1039 bility and flux[62, 72]: $P(E) = \frac{1}{2}(2\pi\hbar)^2 \text{Tr} \left[\hat{F} \delta(E - \hat{H}_N) \hat{F} \delta(E - \hat{H}_N) \right]$ and
1040 $\hat{F} = 1/\hbar \Delta[|0\rangle \langle 1| + |1\rangle \langle 0|]$, respectively. Δ_{if} is a general diabatic coupling
1041 term, which in the Franck-Condon approximation is

$$\begin{aligned}
\Delta_{if} &= \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \sum_{kl} |\langle \chi_k | \chi_l \rangle|^2 \\
&= |V_{if}|^2 \sum_{kl} |\langle \chi_k | \chi_l \rangle|^2
\end{aligned} \tag{A.7}$$

1042 Following standard thermalized Fermi-golden rule derivation[62, 72, 101]
1043 for a transition between two electronic states gives

$$k_{I \rightarrow F} = \frac{2\pi}{\hbar} \sum_{i \in I, f \in F} k_{i \rightarrow f} \tag{A.8a}$$

$$\begin{aligned}
k_{i \rightarrow f} &= \frac{|V_{if}|^2}{\sum_l \exp[-E_{i,l}]} \sum_{lk} \exp[-E_{i,l}] |\langle \chi_k | \chi_l \rangle|^2 \times \delta(E_i - E_f + E_l - E_k) \\
&= |V_{if}|^2 F(E_i - E_f)
\end{aligned} \tag{A.8b}$$

1044 where $F(E_i - E_f)$ is the thermally averaged Franck-Condon factor. If the
1045 nuclear wave functions are taken to be those of a harmonic oscillator, the
1046 Marcus barrier and the rate constant can be obtained from the derivation
1047 in Appendix C. Note that transition between all one electron orbitals are
1048 considered here.

1049 To obtain the DOS-model for electron transfer, only a subset of the transi-
 1050 tion rates is considered. Intuitively, for an reduction of a molecule, transitions
 1051 from the localized occupied metal orbitals to empty orbitals localized at the
 1052 molecule should be considered. This leads to

$$\begin{aligned}
 k_{red} &= \frac{2\pi}{\hbar} \sum_{i \in \text{filled}} \sum_{f \in \text{empty}} k_{i \rightarrow f} \\
 &= \frac{2\pi}{\hbar} \sum_{f \in \text{empty}} \int d\epsilon_i \rho(\epsilon) f(\epsilon - \epsilon_F) k_{i \rightarrow f}
 \end{aligned}
 \tag{A.9}$$

1053 where the second equation highlights the close correspondence with the
 1054 DOS method (Eq. (A.1)), $\rho(\epsilon)$ is the DOS and f the Fermi-Dirac distribu-
 1055 tion. Note also that the PEC method uses a Hamiltonian similar diabatic
 1056 Hamiltonian here. In PEC the total transition probabilities from initial to
 1057 final state are also computed using orbital-to-orbital formulation described
 1058 above.

1059 *Appendix A.3. Choosing the orbitals*

1060 Both DOS and PEC share a fundamental open question: how does one
 1061 choose the localized and empty/filled orbitals? This situation is faced in a
 1062 typical first-principles calculations, where (canonical) one electron orbitals
 1063 are highly delocalized even when charge-localized diabatic states are used,
 1064 making the choice of active orbitals difficult. An important result learned
 1065 from orbital localization methods[150–153] is that the energy from a sin-
 1066 gle determinant method such as DFT or Hartree-Fock methods is invariant
 1067 to orbital rotation within the *occupied molecular orbitals*. Thus, occupied
 1068 orbitals can be localized using a unitary rotation which leaves *the energy,*
 1069 *and the total wave function unchanged*; during this process the spatial shape
 1070 and spread of filled one electron orbitals are drastically changed. Also, the
 1071 empty, virtual orbitals can be localized separately. However, the filled and
 1072 empty are not allowed to mix during the localization to avoid changes in
 1073 occupation of numbers[154]. As mixing is forbidden, orbital localization is
 1074 performed separately for the empty and filled orbitals and consequently two
 1075 different unitary transforms are required.

1076 A concrete example helps to understand why the orbital localization cause
 1077 practical difficulties. Consider for example an outer-sphere ET from an elec-
 1078 trode to O₂ forming a superoxide species. Here the initial state wave functions

1079 $\{|I\rangle\}$ would be occupied orbitals localized on the metal and the final state
 1080 orbitals $\{|F\rangle\}$ would be empty states localized on O_2 . After a normal DFT
 1081 calculation, one performs a unitary transform on both the initial and final
 1082 states separately such that the the orbitals are well localized to the molecule
 1083 and metal for both states: $|I\rangle = \hat{U} |I_{DFT}^{filled}\rangle$ and $|F\rangle = \hat{V} |F_{DFT}^{empty}\rangle$, with
 1084 $\hat{U}\hat{U}^\dagger = 1$ and $\hat{V}\hat{V}^\dagger = 1$. Note that nuclear wave function remain unchanged
 1085 as the electronic energy is unaffected by the transformation. Thus, the uni-
 1086 tary transformation leaves the thermally averaged Franck-Condon weight
 1087 unchanged.

1088 However, the electronic coupling elements for a given $V_{if} = \langle i|\hat{H}|f\rangle$
 1089 change drastically as the electronic orbitals are rotated. This is easily seen
 1090 from the close correspondence[155] between the coupling and overlap ele-
 1091 ments $\langle i|V|f\rangle \approx v \langle i|f\rangle$, where v is a constant. Changing from the localized
 1092 to delocalized states is written as $\langle i|f\rangle = \langle i_{dft}|\hat{U}^\dagger\hat{V}|f_{dft}\rangle \neq \langle i_{dft}|f_{dft}\rangle$ when
 1093 final (empty) and initial (filled) canonical DFT orbitals are localized sepa-
 1094 rately. Only when $\hat{U} = \hat{V}$ is the overlap between the localized and canon-
 1095 ical orbitals the same; this would require of mixing of the filled and empty
 1096 canonical orbitals resulting in changes in the total energy and the total wave
 1097 function and is therefore discouraged.

1098 As a concrete example consider Eq. (A.9) where only states below the
 1099 Fermi-level contribute to the reduction rate. As potential is changed, some
 1100 orbitals become empty or occupied changing the driving force of the reac-
 1101 tion which remains unchanged under the orbital localization. The rate is
 1102 dictated by transition probability directly related to the matrix elements in
 1103 non-adiabatic reactions. *Thus, the rate of non-adiabatic electron transfer re-*
 1104 *action depends on how the orbitals are chosen and localized.* This can lead
 1105 to inconsistent and incorrect interpretation of the electrochemical rate as a
 1106 function of the potential if basic single determinant methods are used to
 1107 parametrize the DOS or PEC models. Great care is needed when the meth-
 1108 ods and as emphasized in Ref. 82 "this is not a failure of the computational
 1109 methods used but is a consequence of how the rate constant is defined by
 1110 the phenomenological equations. It is therefore important to choose the ap-
 1111 proach which is equivalent to the experiment or thought experiment that the
 1112 theory is attempting to reproduce".

1113 Based on the above discussion, a very important conclusion is reached:
 1114 the rate obtained from the Fermi golden rule, DOS or PEC using only the
 1115 "active orbitals" depend on the way the orbitals are localized. Therefore,

1116 one needs to acknowledge that orbital localization needed when the orbital-
 1117 based models are parametrized using canonical DFT methods, leads to arbitrary
 1118 changes in the rate constant depending on the localization or rotation
 1119 used scheme. Hence, while the energy, density, and the total wave function
 1120 remain unchanged after a unitary transformation of the orbitals, single
 1121 orbitals and single orbital overlaps will necessarily be affected. Therefore, a
 1122 unitary transformation such as orbital localization will unphysically affect the
 1123 rate obtained from methods using one-electron orbitals and orbital-to-orbital
 1124 transitions to compute the transition probability. If one electron-based the
 1125 DOS or PEC methods are parametrized using first-principles approaches,
 1126 methods such as fragment orbital DFT[156] methods might be applicable.

1127 Care is also required when using many-body wave functions for computing
 1128 the rates. While unitary transform does not change any observables of
 1129 a single diabatic wave function, the off-diagonal matrix elements might be
 1130 sensitive to orbital rotations. However, in approaches such constrained DFT
 1131 employed in this work, the coupling elements are functionals of the electron
 1132 densities of the initial and final state[96] and as such in principle unaffected
 1133 by orbital localization.

1134 **Appendix B. Grand canonical formulation for electrochemical systems** 1135 **tems**

1136 Below the necessary details for grand canonical formalism are presented.
 1137 A more complete treatment is given in Ref. 3.

Within GCE all expectation values are computed using

$$\langle O \rangle = \text{Tr} \left[\hat{\rho} \hat{O} \right] \quad (\text{B.1})$$

with the grand canonical density operator

$$\hat{\rho} = \frac{\exp \left[-\beta (\hat{H}_{tot} - \sum_i \tilde{\mu}_i \hat{N}_i) \right]}{\text{Tr} \left[\exp \left[-\beta (\hat{H}_{tot} - \sum_i \tilde{\mu}_i \hat{N}_i) \right] \right]} \quad (\text{B.2})$$

1138 where \hat{H}_{tot} is the Hamiltonian, $\tilde{\mu}_i$ is the electrochemical potential of
 1139 species i , and \hat{N}_i is the number operator. The partition function is defined
 1140 as $\Xi = \text{Tr} \left[\exp \left[-\beta (\hat{H}_{tot} - \sum_i \mu_i \hat{N}_i) \right] \right]$ from which the grand free energy is

1141 $\Omega[T, V, \mu] = -k_B T \ln \Xi = E - TS - \sum_i \mu_i N_i$. The probability of being in
 1142 microstate i is

$$p_i^{GC} = \frac{\exp \left[-\beta \langle \Psi_i | \hat{H}_{tot} - \sum_j \tilde{\mu}_j \hat{N}_j | \Psi_i \rangle \right]}{\Xi} \quad (\text{B.3})$$

1143 In the above equation, $|\Psi_i\rangle$ is the total wave function of both the electrons
 1144 and nuclei so that the particle number operators \hat{N}_i corresponds to electrons
 1145 or the nuclear identities as specified below. With these definitions fixed
 1146 potential, grand canonical can be computed. For example, the grand energy
 1147 for electrons n and electrolyte \pm with fixed chemical potential is is given by

$$\begin{aligned} \Omega(T, V, \tilde{\mu}_{\pm}, \tilde{\mu}_n) &\equiv \sum_i p_i \left[\beta \ln p_i + \langle \Psi_i | \hat{H}_{tot} - \mu_{\pm} (\hat{N}_+ + \hat{N}_-) - \tilde{\mu}_n \hat{N}_n | \Psi_i \rangle \right] \\ &= \text{Tr} \left[\hat{\rho} \hat{\Omega} \right] \equiv \Omega[\hat{\rho}] \end{aligned} \quad (\text{B.4})$$

1148 Appendix C. Adiabatic and non-adiabatic harmonic TST rates

1149 Here classical harmonic TST (HTST) for adiabatic and non-adiabatic
 1150 reactions within GCE are derived.

1151 Appendix C.1. Adiabatic HTST

1152 The general TST rate equation is shown in Eq. (7). First, consider
 1153 a general case where potential the number of both nuclei and electrons is
 1154 allowed to fluctuate. Usually, for N_N classical nuclei the Hamiltonian in mass-
 1155 weighted coordinates (\mathbf{x}_i) and momenta P_i is written as $H_{cl} = \sum_{i \in N_N} P_i^2 +$
 1156 $V(\mathbf{x}_i)$. $V(\mathbf{x}_i)$ defines the (Born-Oppenheimer) potential energy surface.

1157 Then consider a system is open to electrons at a fixed electron chemi-
 1158 cal potential while number of nuclei is fixed. Also, the system is assumed
 1159 adiabatic meaning that the number and distribution of electrons adjusts in-
 1160 stantaneously to the nuclear configuration. This is the common situation
 1161 considered in first principles calculations at fixed electrode potential cal-
 1162 culations. For this case, the Kohn-Sham-Mermin theorem guarantees that
 1163 electronic energy and distribution are unique to a given electron chemical
 1164 potential and external potential (here provided by the nuclei). Hence, the
 1165 potential energy V is not only a parametric function of the nuclear positions

1166 but also the chemical potential of the electrons. Furthermore, as shown in
 1167 Ref. 3, the grand free energy of the electrons is given by $\Omega_n(T, V, N_N, \mu_n; \mathbf{x}_i)$.
 1168 As the nuclei move on the effective potential energy surface provided by
 1169 the electrons, one recognizes that $V(\mathbf{x}_i, \mu_n) = \Omega_n(T, V, N_N, \mu_n; \mathbf{x}_i)$ (see Ref.
 1170 3 and Appendix B). Then, for the open electronic system, the classical
 1171 Hamiltonian for the nuclei is

$$H(N_N)_{cl} = \sum_{i \in N_N} P_i^2 + V(\mathbf{x}_i, \mu_n) \equiv H_{cl} \quad (\text{C.1})$$

1172 where I and \ddagger denote the initial and transition states. The TST rate is
 1173 written as [101]

$$k_{TST}(N_N, V, T)Q_I = \int_N dP \int_N d\mathbf{x} \exp\left[-H_{cl}^\ddagger \beta\right] \delta(f(\mathbf{x})) (\nabla f \cdot P^N) h(\nabla f \cdot P^N) \quad (\text{C.2})$$

1174 where f is the $N - 1$ dimensional dividing surface between the reactants
 1175 and products, $\nabla f \cdot P^N = P_{n^\ddagger}$ is the momentum normal to f identified as
 1176 the reaction coordinate, $h(\nabla f \cdot P^N) = h(P_{n^\ddagger})$ is a step function separating
 1177 the reactant and product basins, and $\delta(f(x^N))$ restricts the geometries to lie
 1178 on the dividing surface. With these definitions the canonical HTST at fixed
 1179 electron chemical potentials follows from:

$$\begin{aligned} k_{HTST}(T, V, N_N) &= \int_N dP \int_{N-1} d\mathbf{x} P_{n^\ddagger} \frac{\exp\left[-H_{cl}^\ddagger \beta\right]}{Z_I} \\ &= \frac{\int_N dP \int_{N-1} d\mathbf{x} P_{n^\ddagger} \exp\left[-\beta(\sum_{i=0}^N 1/2P_i^2 + V(\mathbf{x}_i, \mu_n)^\ddagger)\right]}{\int_N dP \int_N d\mathbf{x} \exp\left[-\beta(\sum_{i=0}^N 1/2P_i^2 + V(\mathbf{x}_i, \mu_n)^I)\right]} \\ &= \frac{1}{\sqrt{2\pi\beta}} \frac{\int_{N-1} d\mathbf{x} \exp\left[-\beta V(\mathbf{x}_i, \mu_n)^\ddagger\right]}{\int_N d\mathbf{x} \exp\left[-\beta V(\mathbf{x}_i, \mu_n)^I\right]} \\ &\approx \frac{v_N}{\sqrt{2\pi}} \frac{\prod_i^{N-1} v_i}{\prod_i^{N-1} v_i^\ddagger} \exp\left[-\beta(\Omega_n^\ddagger - \Omega_n^I)\right] \\ &= \frac{v_N}{2\pi} \exp\left[-\beta(\Omega_N^\ddagger - \Omega_N^I)\right] = \frac{v_N}{2\pi} \exp\left[-\Delta\Omega_N^\ddagger \beta\right] \end{aligned} \quad (\text{C.3})$$

1180 where at the second last row the effective potentials are Taylor expanded
 1181 in terms of normal mode coordinates with corresponding frequencies v_i and

1182 v_N is the frequency along the reaction coordinate: $V^{\ddagger/I} = \Omega_N^{\ddagger/I} + 1/2 \sum_i v_i q_i^2$.
 1183 The last equality follows from setting the nuclear vibrational entropy $S_N =$
 1184 $k_B \ln \left(\prod_i^{N-1} v_i / \prod_i^{N-1} v_i^{\ddagger} \right)$ and setting the total grand free energy to $\Omega_N =$
 1185 $\Omega_n - TS_N$. Here the subscript N reminds that the number of nuclei was kept
 1186 fixed above. **Note that Eq. (C.3) would be used in typical first prin-**
 1187 **ciples calculations at fixed electrode potentials where the electron**
 1188 **chemical potential and number of nuclei are fixed.**

1189 The above treatment can also be extended to treat situations in which
 1190 both the number of electrons and nuclei are allowed to fluctuate. This is
 1191 straight-forward and can be obtained by. Inserting Eq. (C.3) in (7) and
 1192 applying Eq. (8) leads to

$$k_{HTST}(T, V, \mu) = \frac{\langle v_N \rangle_{\mu}}{2\pi} \exp[-\Delta\Omega^{\ddagger}\beta] \quad (\text{C.4})$$

1193 where $\langle v_N \rangle_{\mu}$ is the effective frequency along the reaction coordinate com-
 1194 puted using effective fixed potential PESs.

1195 *Appendix C.2. Non-adiabatic HTST*

1196 Next, non-adiabatic harmonic transition state theory (NA-HTST) ap-
 1197 proximation to the rate is developed. Unlike for the canonical case, only a
 1198 fixed number of nuclei is treated. NA-HTST also requires the calculation
 1199 of matrix elements $H_{AB} = \langle \Psi_A | \hat{H} | \Psi_B \rangle$. These H_{AB} s are defined only when
 1200 $|\Psi_A\rangle$ and $|\Psi_B\rangle$ have the same number of both electron and nuclei. Also,
 1201 the adiabatic approximation cannot be used and the electrons do not in-
 1202 stantaneously adapt to nuclear positions. Hence, unlike for the adiabatic
 1203 case, constant electron number $V(x, n)$ rather than constant electron poten-
 1204 tial $V(x, \mu_n)$ is used. The appropriate Hamiltonian is given by Eq. (A.6), in
 1205 which $H_{cl} = \sum_{i \in N_N} P_i^2 / 2m_i + V_i(\mathbf{x}_i)$.

1206 Using this Hamiltonian, assuming a quadratic potential V and applying
 1207 the Golden rule form the basis for NA-HTST. This derivation can be found in
 1208 *e.g.* Ref 74. Another path, presented below, is to use the classical transitions
 1209 state theory using the Landau-Zener transition P_r probability[100, 101] and
 1210 assuming that the potential energies are quadratic. Then, the following iden-
 1211 tities are used: The reorganization energy and vibrational frequency along
 1212 the reaction coordinate are related as $\lambda = 2v_N^2 \Delta q^2 = 2mv_N^2 \Delta x^2$, where Δq
 1213 and Δx are the geometric differences of the initial and final states in mass
 1214 weighted and cartesian coordinates states, respectively. The differences of

1215 forces can written as gradient of the two parabolas at the transition state
 1216 as shown in Ref. 74 to yield $|\Delta F|_{\ddagger} = \lambda/\Delta x$. With these definitions, fixed
 1217 number (canonical) electronic/nuclear NA-HTST can be derived:

$$\begin{aligned}
 k_{HTST}^{na}(T, V, N_N, N_n) &= \int_N dP \int_{N-1} d\mathbf{x} P_r P_{n^\ddagger} \frac{\exp[-H_{cl}^\ddagger \beta]}{Z_I} \\
 &= \int_N dP \int_{N-1} d\mathbf{x} \left(1 - \exp\left[-\frac{2\pi|H_{IF}|^2}{\hbar|P_{n^\ddagger} \nabla_{n^\ddagger}(V_I - V_F)|}\right] \right) P_{n^\ddagger} \frac{\exp[-H_{cl}^\ddagger \beta]}{Z_I} \\
 &\stackrel{\text{linearize exp}}{\approx} \int_N dP \int_{N-1} d\mathbf{x} \frac{2\pi|H_{IF}|^2}{\hbar|P_{n^\ddagger} \nabla_{n^\ddagger}(V_I - V_F)|} P_{n^\ddagger} \frac{\exp[-H_{cl}^\ddagger \beta]}{Z_I} \\
 &\stackrel{\text{forces}}{=} \int_N dP \int_{N-1} d\mathbf{x} \frac{2\pi|H_{IF}|^2}{\hbar P_{n^\ddagger} |\Delta F|} P_{n^\ddagger} \frac{\exp[-H_{cl}^\ddagger \beta]}{Z_I} \\
 &\stackrel{\text{integrate } P}{=} \frac{2\pi|H_{IF}|^2}{\hbar|\Delta F|} \frac{\int_{N-1} d\mathbf{x} \exp[-V^\ddagger \beta]}{\int_N d\mathbf{x} \exp[-V_I \beta]} \\
 &\stackrel{\text{harmonic TST}}{\approx} \sqrt{2\pi\beta} \frac{|H_{IF}|^2}{\hbar|\Delta F|} v_N \frac{\prod_i^{N-1} v_i}{\prod_i^{N-1} v_i^\ddagger} \exp[-(E^\ddagger - E_I)\beta] \\
 &\stackrel{\text{vib. entropy}}{=} \sqrt{2\pi\beta} \frac{|H_{IF}|^2}{\hbar|\Delta F|} v_N \exp[-\Delta A^\ddagger \beta] \\
 &\stackrel{|\Delta F|_{\ddagger} = \lambda/\Delta x}{\approx} \sqrt{2\pi\beta} \frac{\sqrt{m} v_N \Delta x |H_{IF}|^2}{\hbar \lambda} \exp[-\Delta A^\ddagger \beta] \\
 &\stackrel{\lambda = 2mv_N^2 \Delta x^2}{=} \sqrt{\frac{\pi\beta}{\hbar^2 \lambda}} |H_{IF}|^2 \exp[-\Delta A^\ddagger \beta] \\
 &\stackrel{\text{Marcus barrier}}{\approx} \sqrt{\frac{\pi\beta}{\hbar^2 \lambda}} |H_{IF}|^2 \exp\left[-\beta \frac{(\Delta A^0 + \lambda)^2}{4\lambda}\right]
 \end{aligned} \tag{C.5}$$

1218 The above rate is derived for fixed number of electrons and nuclei. As
 1219 done for the adiabatic case, this fixed particle rate needs to be turned to
 1220 a fixed potential rate. In particular, the electronic subsystem needs to be
 1221 open in order to study kinetics at a fixed electrode potential. However, gen-
 1222 eralization of the NA-HTST to GCE is significantly more difficult compared
 1223 the the adiabatic as discussed. The electronically GCE NA-HTST can be
 1224 accomplished the approach in Section 4 resulting in Eqs. (40) and (48).

1225 To gain more insight, it is useful to compare the above derivation to the
 1226 GCE-EVB picture used for deriving the GCE equivalent of Marcus barriers
 1227 i.e. Eq. (18). Using Eq. (8) with the GCE Marcus barrier of Eq. (18) with
 1228 an effective non-adiabaticity correction gives

$$k_{HTST}^{na}(T, V, N_N, \mu_n) \approx \left\langle \sqrt{\frac{\pi\beta}{\hbar^2\lambda}} |H_{IF}|^2 \right\rangle_{\mu_n} \exp\left[-\beta \frac{(\Delta\Omega_{FI} + \Lambda)^2}{4\Lambda}\right] \quad (\text{C.6})$$

1229 where the prefactor is computed for either i) some particle number and
 1230 assumed to independent of the electrode potential or ii) various particle num-
 1231 bers and weighted according to the grand canonical distribution.

1232 Appendix D. Grand canonical perturbation theory

1233 If only the electronic subsystem is open, the easiest approach is to use
 1234 an effective fixed electrode potential Hamiltonian like the one introduced in
 1235 Eq. (C.1). Then, one solves equations similar to (10) using this effective
 1236 constant potential Hamiltonian to obtain fixed (electrode) potential diabatic
 1237 states. Then, the diabatic states and grand energy curves are computed
 1238 along the reaction coordinate. From the curve crossing point an estimate for
 1239 the constant (electrode) potential grand energy barrier is obtained.

1240 To keep the present work as general as possible *i.e.* allowing both the
 1241 number of electron and nuclear species to fluctuate, a simple effective Hamil-
 1242 tonian cannot be specified. Instead, explicitly sampling the GCE and number
 1243 of electrons and nuclei is needed. In this case, one can follow and extend the
 1244 general thermodynamic perturbation theory of Zwanzig[104] to GCE. Along
 1245 these lines, the canonical energy operator $H = H_0 + V$ is defined and par-
 1246 titioned to contributions from the unperturbed H_0 part and a perturbation
 1247 V . The total GC partition function Ξ and grand energy Ω are given by (see
 1248 Appendix B)

$$\Xi = \text{Tr}[H - TS - \mu N] \quad \text{and} \quad \exp[-\beta\Omega] = \Xi \quad (\text{D.1})$$

1249 Then, the total grand energy can be multiplied and divided by the un-
 1250 perturbed grand energy

$$\exp[-\beta\Omega] = \frac{\exp[-\beta(\Omega - \Omega_0)]}{\exp[-\beta\Omega_0]} = \frac{\exp[-\beta(\Omega_V)]}{\exp[-\beta\Omega_0]} = \langle \exp[-\beta V] \rangle_0 \quad (\text{D.2})$$

1251 where the last identity means that the perturbation part of the grand
 1252 energy is obtained by performing an GCE sampling of the perturbation part.
 1253 For electron transfer reactions, the total Hamiltonian can be written as[157]

$$H = K + U + V_x \quad (\text{D.3})$$

1254 where K is the kinetic energy, U is the interaction energy and V_x is the
 1255 perturbation which depends on extent of the reaction: $x = 0$ and $x = 1$
 1256 correspond to initial and final states, respectively. A linear switch from the
 1257 initial to the final state is obtained by $V_x = V_I - x(V_F - V_I)$. This potential
 1258 defines the initial and final diabatic states and based on the energies of the
 1259 initial and final states E_I and E_F , one defines the instantaneous energy gap
 1260 $\Delta E(R) = E_F(R) - E_I(R) = X$ at geometry R . As noted by Zusman[98] and
 1261 Warshel[99] (see also Ref. 158 for a combined discussion), the energy gap
 1262 coordinate is directly related to the (solvent/bath) reorganization coordinate
 1263 and both are often used in deriving electron transfer rates. It was recently
 1264 shown by Jeanmairet *et.al.*[157] that the energy gap coordinate is a valid
 1265 reaction coordinate also within GCE.

Combining the two state GCE diabatic model for the initial I and final F states with the general perturbation result, one obtains,

$$\begin{aligned} \exp[-\beta\Delta\Omega] &= \frac{\langle \exp[-\beta V_F] \rangle_F}{\langle \exp[-\beta V_I] \rangle_I} \\ &= \frac{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta V_F}}{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta V_I}} = \frac{\Xi_F^V}{\Xi_I^V} \end{aligned} \quad (\text{D.4})$$

1266 which gives $\Delta\Omega = -\beta^{-1} \ln(\Xi_F^V/\Xi_I^V)$. Next, the sampling is constrained to
 1267 a specific region of the energy gap. As recently shown in Ref. 157, a one-to-
 1268 one mapping exists between the vertical energy gap $\langle \Delta E \rangle_x$, x , the potential
 1269 V_x , and the probability (p_x) of being in microstate sampled from the GCE:
 1270 $x \leftrightarrow \langle \Delta E \rangle_x \leftrightarrow V_x \leftrightarrow p_x$. Introducing the energy gap coordinate and noting
 1271 that the energies of I and F are computed from the same Hamiltonians
 1272 except for the "perturbation" part, allows writing

$$\begin{aligned} \Delta\Omega &= -\beta^{-1} \ln \left(\frac{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta(\Delta E + V^I)}}{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta V^I}} \right) = \\ &= -\beta^{-1} \ln \langle e^{-\beta\Delta E} \rangle_I = \beta^{-1} \ln \langle e^{\beta\Delta E} \rangle_F \end{aligned} \quad (\text{D.5})$$

1273 where $\Delta E = V_F - V_I$ is used. One can also obtain a probability distribu-
 1274 tion for the energy gap by performing constrained sampling[101] of the grand
 1275 energy curves

$$\bar{\Xi}^i(X) = \sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta E_i} \delta(\Delta E(R) - X) \quad (\text{D.6a})$$

$$p^i(X) = \frac{\bar{\Xi}^i(X(R))}{\bar{\Xi}^i} = \frac{\langle \delta(\Delta E(R) - X) \rangle_i}{\sum_N e^{\beta\mu N} \int dR^N dP^N \delta(\Delta E(R) - X) e^{-\beta E_i}} \quad (\text{D.6b})$$

$$\frac{\sum_N e^{\beta\mu N} \int dR^N dP^N \delta(\Delta E(R) - X) e^{-\beta E_i}}{\sum_N e^{\beta\mu N} \int dR^N dP^N e^{-\beta E_i}}$$

1276 so that $\bar{\Xi}^i = \int dX \bar{\Xi}^i(X) \equiv e^{-\beta\Omega^i}$ and $\Omega^i(X) = -\beta^{-1} \ln(p^i(X)) + \Omega^i$. Above
 1277 Ω^i is the diabatic grand energy and $i = I$ or F . Using the last identity and
 1278 observing that integration over the probability is unity, leads to

$$\Omega^i = -\beta^{-1} \ln \int dX e^{-\beta\Omega^i(X)} \quad (\text{D.7})$$

1279 To arrive at an important identity linking the diabatic grand energies to
 1280 the energy gap is obtained by using the energy gap as the reaction coordinate
 1281 X after writing

$$\begin{aligned} \bar{\Omega}_I(\Delta E) &= -\beta^{-1} \ln(\bar{\Xi}_I(\Delta E)) = \\ &= -\beta^{-1} \ln \left(\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta E_I(R^N)} \delta(\Delta E(R^N) - \Delta E) \right) \\ &= -\beta^{-1} \ln \left(\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta(E_F(R^N) - \Delta E(R))} \delta(\Delta E(R^N) - \Delta E) \right) \\ &= -\beta^{-1} \ln \left(e^{\beta\Delta E} \sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta(E_F(R^N))} \delta(\Delta E(R^N) - \Delta E) \right) \\ &= -\Delta E - \beta^{-1} \ln \left(\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta E_F(R^N)} \delta(\Delta E(R^N) - \Delta E) \right) \\ &= -\Delta E + \bar{\Omega}_F(\Delta E) \end{aligned} \quad (\text{D.8})$$

1282 At this point all relevant free energy identities within the GCE corre-
 1283 sponding to the commonly used identities used for deriving the canonical

1284 Marcus theory have been derived.[99, 105–110] Refs. 99, 105–110 show var-
 1285 ious ways to obtain the iconic canonical Marcus rate constant. To arrive at
 1286 the corresponding rate constant in the GCE, it is shown that detailed bal-
 1287 ance is satisfied. At the transition state the initial and final diabatic grand
 1288 energies are equal giving

$$\begin{aligned}
 \Omega_I(\Delta E^\ddagger) &= \Omega_F(\Delta E^\ddagger) \\
 &\rightarrow -\beta^{-1} \ln(p_I(\Delta E^\ddagger)) + \Omega_I = -\beta^{-1} \ln(p_F(\Delta E^\ddagger)) + \Omega_F \\
 &\rightarrow \frac{p_I(\Delta E^\ddagger)}{p_F(\Delta E^\ddagger)} = \exp[-\beta(\Omega_F - \Omega_I)] = \exp[-\beta\Delta\Omega_{FI}]
 \end{aligned} \tag{D.9}$$

1289 which shows that detailed balance is satisfied. The diabatic grand energy
 1290 surfaces are computed from the energy gap distribution[109]

$$\begin{aligned}
 g_I(\Delta E) &= -\beta^{-1} \ln(p_I(\Delta E)) \quad \text{and} \\
 g_F(\Delta E) &= -\beta^{-1} \ln(p_F(\Delta E)) + \Delta\Omega_{FI}
 \end{aligned} \tag{D.10}$$

1291 The transition state can then be identified from the intersection of the
 1292 relative grand energy curves: $g_I(\Delta E^\ddagger) = g_F(\Delta E^\ddagger)$. Computing the reaction
 1293 rate using the standard transition state theory expression gives

$$k_{IF} = \kappa \frac{\exp[-\beta g_I(\Delta E^\ddagger)]}{\int d\Delta E \exp[-\beta g_I(\Delta E)]} = \kappa p_I(\Delta E^\ddagger) \tag{D.11}$$

1294 showing that the reaction rate is determined by the energy gap distribu-
 1295 tion function $p^I(\Delta E) = \langle \delta(\Delta E(R) - \Delta E) \rangle_I$ from Eq. (D.6). Note, that mi-
 1296 croscopic reversibility is satisfied by construction. To obtain the iconic Mar-
 1297 cus rate within GCE, one may follow the perturbation theory route[104, 109]
 1298 and perform a cumulant expansion on the energy gap distribution as was
 1299 done also when deriving the GCE-NATST in this work in section 4. It has
 1300 been shown in several previous studies[106, 109, 121] that the second order
 1301 cumulant expansion results a Gaussian form for the energy gap distribution

$$p_I(\Delta E) = \frac{1}{\sqrt{2\pi\sigma_I}} \exp\left[-\frac{(\Delta E - \langle \Delta E \rangle_I)^2}{2\sigma_I^2}\right] \tag{D.12}$$

1302 where $\langle \Delta E \rangle_I$ is the energy gap expectation value in the initial state ob-
 1303 tained from Eq. (D.6) and $\sigma_I = \langle (\Delta E)^2 \rangle_I - (\langle \Delta E \rangle_I)^2$ is the gap variance.

1304 The Marcus relation is then obtain after standard manipulations[100, 106]
 1305 by inserting these relations in Eq. (D.8) result in the GCE Marcus rate of
 1306 Eq. (18)

1307 **Appendix E. Thermodynamic analysis of outer-sphere ET in macro-**
 1308 **scopic systems**

1309 Consider a general outer-sphere ET reaction $e^-(M) + B(sol) \rightleftharpoons B^-(sol)$
 1310 where an electron is transferred from the metal (M) to molecule B in the
 1311 solution phase (sol). The equilibrium potential is E^{eq} . Changing the po-
 1312 tential from E_{eq} to E i.e. introducing the over-potential $\eta = E - E^{eq}$
 1313 changes the electron energy by $\Delta\mu_e = -\eta$ for the initial state. The en-
 1314 ergy of the final state changes as $\Delta\mu_{B^-}^{sol} = -F\Delta\phi_{sol}(\eta)$ where ϕ_{sol} is the
 1315 electrostatic potential in the solution phase. The reaction energy is changed
 1316 by $\Delta A = -[\Delta\phi_{sol}(\eta) - \eta]$. $\Delta\phi_{sol}(\eta)$ depends roughly linearly on η . Hence,
 1317 $\Delta A \approx a \times \eta$

1318 **Appendix F. Grand canonical weights as a function of particle**
 1319 **number**

1320 As shown in *e.g.* Eq. (2) or (40), computation of GCE rates involves
 1321 a summation over states with different number of particles. To avoid the
 1322 infinite summation, the crucial question is how many different states are in
 1323 fact needed. This depends on the population probability or weight of different
 1324 particle number states.

1325 Here the weights as a function of μ are studied for a graphene sheet. The
 1326 graphene is modelled using small 4 atom unit cell repeated in the x and y
 1327 directions. The vacuum along the z-directions is 15Å. The GPAW[159–161]
 1328 software is used for the DFT calculations. The grid spacing is set to 0.18Å,
 1329 $16 \times 16 \times 1$ k-point is applied, and exchange-correlation effects are treated
 1330 using the PBE[162] functional. The system is immersed in a continuum
 1331 water solvent using the SCMVD model[163] using the standard parameters
 1332 given in Ref.163. The charged systems are modelled using the homogeneous
 1333 Poisson-Boltzmann model[3, 20] The weights are computed using the usual
 1334 definition:

$$p_N = \frac{\exp[-\beta(E_N - \mu N)]}{\sum_N \exp[-\beta(E_N - \mu N)]} \quad (\text{F.1})$$

Charge	$\mu = E_f$	E	$p(\mu = -4.03 \text{ eV})$	$p(\mu = -3.06 \text{ eV})$
-0.1	-2.46	-37.17	0.0096	0.0536
-0.075	-2.83	-37.11	0.0349	0.1203
-0.05	-3.06	-37.03	0.0988	0.2102
-0.025	-3.53	-36.95	0.2148	0.2825
0	-4.03	-36.86	0.2973	0.2417
0.025	-4.53	-36.75	0.2144	0.1077
0.05	-5.02	-36.63	0.0971	0.0301
0.075	-5.26	-36.50	0.0335	0.0064
0.1	-5.64	-36.36	0.0089	0.0010

Table F.1: Weights for different charge states of graphene as function of μ , the electron chemical potential in eV. E_f is the Fermi-level in eV, E is the total energy, and p are the weights

1335 The results are show in Table F.1. As can be seen the relevant weights
1336 for both $\mu_0 = -4.03$ and $\mu = \mu_0 \pm 0.5eV$ are captured by using 9 charge
1337 states. By carefully choosing the different charge states will reduce the num-
1338 ber needed charge states. Furthermore, larger systems should require less
1339 states as these are "closer" to the thermodynamic limit and the probabilities
1340 approach a Delta function as system size is increased.

1341 Appendix G. Franck-Condon derivation of the non-adiabatic rate

1342 The Franck-Condon treatment starts from the second-last line of Eq. (36)
1343 by noticing that

$$\begin{aligned}
& \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} V_{N,if}^2 \int dt |\langle nN | mN \rangle|^2 e^{it(E_{imN} - E_{fnN})/\hbar} = \\
& \frac{V_{N,if}^2}{2\pi} FC(\Delta E)_i
\end{aligned} \tag{G.1}$$

1344 where $FC(\Delta E)_i$ is the thermalized Franck-Condon factor. In general
1345 case, the thermalized Franck-Condon factor can be computed by Fourier
1346 transforming it and using generating functions.[164] As shown in Ref. 125
1347 chapter 6,the FC-factor can be written using the spectral density function
1348 $J_{fi}(\omega)$ to give

$$\begin{aligned}
FC(\Delta E)_i &= \frac{1}{2\pi\hbar} \exp[G(0)] \int_{-\infty}^{\infty} dt \exp[it\Delta E_{fi}^N/\hbar + G(t)] \\
&\approx \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} \exp\left[it\frac{\Delta E_{fi}^N - \lambda}{\hbar}\right] \exp\left[-\frac{\lambda t^2}{\beta\hbar^2}\right] \\
&= \sqrt{\frac{1}{4\pi k_B T \lambda}} \exp\left[-\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda}\right] \tag{G.2}
\end{aligned}$$

$$\begin{aligned}
\text{where } G(t) &= \int_0^{\infty} d\omega \cos(\omega t) (1 + 2n(\omega)) J_{IF}(\omega) - \sin(\omega t) J_{IF}(\omega) \\
&\approx \int_0^{\infty} d\omega \frac{(\omega t)^2}{\beta\hbar\omega} J_{IF}(\omega) - i \int_0^{\infty} d\omega t \omega J_{IF}(\omega)
\end{aligned}$$

1349 using the high-temperature approximation ($1 + 2n(\omega) \approx 2k_B T \gg 1$)
1350 and slow-fluctuating Debye solvent assumptions and $\int_0^{\infty} d\omega \omega J_{IF}(\omega) = \lambda/2$
1351 has been used. Hence, if the spectral density not sensitive to the number of
1352 electrons, the reorganization energy is independent on the number of elec-
1353 trons in the systems. For practical purposes this is expected to be a good
1354 approximation. When the approximate FC factor is introduced, Eq. (G.1)
1355 gives the Marcus rate in the GCE.

1356 **Appendix H. Decomposition of the reorganization energy to inner- 1357 and outer-sphere contributions**

1358 The total reorganization energy is often[54, 75, 103, 165] modified dif-
1359 ferentiate between inner- and outer-sphere contributions. This is achieved
1360 by partitioning the surrounding molecules to tightly bound ligands or inner-
1361 solvent solvent molecules and the bulk solvent. While this is not necessary
1362 in the approach taken in this work, separating the effect the nearby atoms
1363 or molecules and the solvent might be useful for a understanding the role
1364 of different constituents on the overall reaction. In both computational and
1365 theoretical studies this separation occurs naturally if the bulk solvent is pre-
1366 sented as a continuum as in the work of Dogonadze *et.al.*[49, 50] for ET and
1367 SHS[54] for PCET.

1368 To single out the solvent reorganization energy, a solvent polarization co-
1369 ordinate \mathcal{Q} is introduced. As detailed in Ref. 54 this coordinate introduces a

1370 new parametric dependence to the electron, proton, and vibrational Hamil-
 1371 tonians, wave functions and energies. Here it is shown how an additional
 1372 solvent coordinate modifies the ET reactions and the PCET kinetics can be
 1373 treated analogously.

1374 First, a solvent coordinate \mathcal{Q} is introduced. The solvent coordinate is
 1375 orthogonal to other coordinates which allows writing the wave function as
 1376 $|imaN\rangle = |iN(q, \mathcal{Q})\rangle |mN(\mathcal{Q})\rangle |aN\rangle$ where $|aN\rangle$ is the wave function re-
 1377 lated to solvent polarization. Similarly the energies from Eqs. (42) obtain
 1378 a parametric dependence on \mathcal{Q} . The initial state solvent wave functions are
 1379 eigenfunctions obtained from

$$[\hat{T}_{\mathcal{Q}} + \epsilon_{mN}] |aN\rangle = \mathbb{E}_{aN} |aN\rangle \quad (\text{H.1})$$

1380 and similarly for the final state. Above, $\hat{T}_{\mathcal{Q}}$ is the kinetic energy operator
 1381 for the outer-sphere species. Then the total energy is given by

$$E_{imaN} = \varepsilon_{iN} + \epsilon_{mN}^i + \mathbb{E}_{aN} \quad (\text{H.2})$$

1382 and the total coupling between the initial and final states is

$$\begin{aligned} V_{imaN,fnbN} &= \langle fmbN | \hat{V}_N | imaN \rangle \\ &\approx \langle fN | \hat{V}_N | iN \rangle \langle nN | mN \rangle_q \langle bN | aN \rangle_{\mathcal{Q}} \\ &= V_{if,N} S_{nm,N} \mathcal{S}_{ab,N} \end{aligned} \quad (\text{H.3})$$

1383 Assuming that the outer-sphere free energy related to the solvent reorga-
 1384 nization is independent of the particle number allows separating its contri-
 1385 bution from the total grand partition function

$$\begin{aligned} \Xi_i &= \sum_{m,a,N} \exp[-\beta(E_{imaN} - \mu N)] \\ &\approx Q_a \sum_{m,N} \exp[-\beta(E_{imN} - \mu N)] = Q_a \Xi_{im} \end{aligned} \quad (\text{H.4})$$

1386 Note that inner-sphere energies and partition function explicitly depend
 1387 on the particle number. Inserting the last two equations in the golden rule
 1388 expression yields

$$\begin{aligned}
k &= \frac{2\pi}{\hbar \Xi_i} \sum_{Nabmn} e^{-\beta(\varepsilon_{iN} - \mu N + \beta \mathbf{E}_{aN}^i + \varepsilon_{mN})} \left| \langle Nn\upsilon f | \hat{V}_N | iumN \rangle \right|^2 \delta(E_{imaN} - E_{fnbN}) \\
&\approx \frac{2\pi}{\hbar} \sum_N \sum_{m,n} p_{imN} \sum_{a,b} p_{aN} V_{if,N}^2 S_{nm,N}^2 \mathcal{S}_{ab,N}^2 \delta(E_{imaN} - E_{fnbN})
\end{aligned} \tag{H.5}$$

1389 where $p_{imN} = \exp[-\beta(\varepsilon_{iN} + \varepsilon_{mN} - \mu N)]/\Xi_{im}$ and $p_{aN} = \exp[-\beta \mathbf{E}_{aN}/Q_a]$.
1390 As done above, representing the delta function as a Fourier transform allows
1391 writing

$$\begin{aligned}
k &= \sum_N \frac{V_{if,N}^2}{\hbar^2} \int dt \langle e^{it(\varepsilon_{mN}/\hbar} e^{-it(\varepsilon_{nN})/\hbar} \rangle_q \times \langle e^{it(\mathbf{E}_{aN}/\hbar} e^{-it(\mathbf{E}_{bN})/\hbar} \rangle_Q \\
&= \sum_N \frac{V_{if,N}^2}{\hbar^2} \int dt G_{mn,N}(t) g_{ab,N}(t)
\end{aligned} \tag{H.6}$$

1392 where auxiliary correlation functions $G_{mn,N}(t)$ and $g_{ab,N}(t)$ are introduced
1393 providing a connection to the work of SHS[54, 55]. To be specific, $G_{mn,N}(t)$
1394 characterizes the inner-sphere contributions while $g_{ab,N}(t)$ is related to the
1395 outer-sphere solvent polarization. Different approximations for the correla-
1396 tion functions presented by SHS in Ref. 54, 55 can be readily used here
1397 as well to derive various well-defined limits of the rate equation. For ex-
1398 ample, assuming that the intra-molecular modes can be neglected leads to
1399 Eq.(36) with a/b replacing the m/n indices. Within this assumption and
1400 repeating the steps leading to Eq. (40) shows that resulting reorganization
1401 energy is the solvent reorganization energy and the inner-sphere interactions
1402 contribute only to the reaction energy.

1403 If the intra-sphere contributions cannot be neglected, the rate equations
1404 become rather cumbersome in general. However, the case $G_{ab,N}(t) \approx G_{ab}(t)$
1405 *i.e.* that the outer-sphere contribution to rate is independent of the parti-
1406 cle number, deserves some attention. For this, the inner- and outer-sphere
1407 components are separated by rewriting Eq.(H.5) using a convolution[165]

$$k = \sum_N p_{iN} \frac{2\pi V_{if,N}^2}{\hbar} \int dE f(x) F(\Delta E_{fi}^N - x) \tag{H.7}$$

1408 with $f(x) = \sum_{mn} p_{mN} S_{nm,N}^2 \delta(\epsilon_{mN}^i - \epsilon_{nN}^i + E)$ and $F(E_{fi}^N - x) = \sum_{ab} p_{aN} \mathcal{S}_{ab,N}^2 \delta(\mathbb{E}_{aN} -$
1409 $\mathbb{E}_{bN} + \Delta E_{fi}^N - x)$ as shown for single N in Ref.165. $f(x)$ and $F(E_{fi}^N - x)$ rep-
1410 resent inner- and outer-sphere contributions to transition probability. Again
1411 various forms for both terms can be derived[165]. To retain consistency, a
1412 high-temperature approximation for quadratic solvent modes is used. This
1413 gives[54, 55, 165]

$$F(E_{fi}^N - x) = \frac{1}{\hbar \sqrt{4\pi k_B T \lambda_o^N}} \exp \left[-\frac{(\Delta E_{fi}^N + \lambda_o^N)^2}{4k_B T \lambda_o^N} \right] \quad (\text{H.8a})$$

$$f(x) = FC(\Delta E - x)_i \quad (\text{H.8b})$$

1414 where $FC(\Delta E - x)_i$ is a modified Franck-Condon factor given in (G.2)
1415 and λ_o^N is recognized as the outer-sphere reorganization energy. Making the
1416 high-temperature and slow-fluctuating Debye solvent approximations as done
1417 in Eq (G.2) allows performing the convolution integral. This yields [165]

$$k = \sum_N p_{iN} \frac{2\pi V_{if,N}^2}{\hbar} \frac{1}{\hbar \sqrt{4\pi k_B T (\lambda_o^N + \lambda_i^N)}} \exp \left[-\frac{(\Delta E_{fi}^N + \lambda_o^N + \lambda_i^N)^2}{4k_B T (\lambda_o^N + \lambda_i^N)} \right] \quad (\text{H.9})$$

1418 Finally the assumption that the outer-sphere contributions do not depend
1419 on the particle number can be applied to give

$$k = \sum_N p_{iN} \frac{2\pi V_{if,N}^2}{\hbar} \frac{1}{\hbar \sqrt{4\pi k_B T (\lambda_o + \lambda_i^N)}} \exp \left[-\frac{(\Delta E_{fi}^N + \lambda_o + \lambda_i^N)^2}{4k_B T (\lambda_o + \lambda_i^N)} \right] \quad (\text{H.10})$$

1420 From this form it can be seen that the total reorganization energy can
1421 be separated to a particle number independent solvent contribution λ_o and
1422 a reorganization energy of the inner sphere component λ_i^N which depends
1423 explicitly on the particle number.

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