On the fundamentals of quantum rate theory and the long-range electron transport in respiratory chains

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This document corresponds to the **Supplementary Document** of the manuscript entitled *On the Fundamentals of Quantum Rate Theory and the Long-range Electron Transport in Respiratory Chains*, Chemical Review Society, a Journal of the Royal Society of Chemistry.

1. THE MEANING OF QUANTUM AND ELECTROCHEMICAL CAPACITANCES

The meaning of the quantum capacitance (also referred as chemical capacitance [1]) is related to the potential energy difference $-eV$ associated with D (HOMO, Highest Occupied Molecular Orbital) and A (LUMO, Lowest Unoccupied Molecular Orbital) chemical energy states within an electrodynamics of transmittance between these states, which can occur inter or intra molecules. Accordingly, these corresponding $-eV$ differences are inversely dependent on the density-of-state (dn/dE), such as that $-eV = e^2/C_q = (dE/dn)$, where (dE/dn) is the amount of energy per amount of quantum channel modes within the $D - A$ states (of a molecule or in between molecules). Hence, the quantum modes of electron transmittance are formed as a result of the formation of the $D - A$ structures. The latter analysis directly leads to $\mu = (dE/dn) = -eV$, where $\mu = (dE/dn) = \Delta E_{HL}/2$ is identified as the electronic chemical potential [2, 3] of the D or A state and is computed as the halfway energy difference ΔE_{HL} between E_H (HOMO) and E_L (LUMO) energy states, being the free energy per number of elementary charge e required for ET or electron transport to proceed through a quantum channel of length L established between the electronically coupled D and A states. This free energy per electron directly correlates with the conductance quantum, as a key presumption of the quantum rate theory.

Accordingly, the general definition of quantum capacitance depends on identifying the quantum levels and states existing between two different reservoirs (note that D and A states defined in the main text can be considered particular types of electron reservoirs) that are contacted (chemically or physically). Taking the individual electronic structure of D and A separately without establishing, in principle, any type of ET mechanism or electrodynamics occurring between these reservoirs, hence

the quantum capacitance is simply defined as

$$\frac{1}{C_q} = \frac{1}{e^2} \left[\frac{1}{(dn/dE)_D} + \frac{1}{(dn/dE)_A} \right],$$ (S1)

where $(dn/dE)_D$ and $(dn/dE)_A$ are the DOS of D and A reservoirs, respectively.

Note that Eq. S1 is general for any molecular scale and hence C_q cannot be defined for macroscopic entities. For instance, if the general C_q concept stated in Eq. S1 is applied to the separation of an amount of charge q over a potential difference V imposed over two macroscopic metallic plate electrodes, it leads to $e^2/C_q = [1/\text{DOS}_l + 1/\text{DOS}_r]$, where DOS_l and DOS_r are the DOS of the left and right metallic plates, respectively. Because both DOS_l and DOS_r are very high for macroscopic metallic-like reservoirs with very high density-of-states, the energy contribution associated with the occupancy of the states, computed as e^2/C_q, tends to be null, according to Eq. S1, where both $(dn/dE)_l$ and $(dn/dE)_r$ will be very high and thus leading to $e^2/C_q \sim 0$. In other words, macroscopic metallic plates do not contribute with any additional (chemical or quantum) energy contribution besides that associated with the electrostatic coulombic spatial separation of charges owing to the imposed electric potential energy, which is not computed in Eq. S1.

Let us now analyze a particular situation of C_q, as stated in Eq. S1, in which the left plate of a capacitor is a metallic probe whereas the right is formed by an ensemble of molecules in contact with the left macroscopic metallic contact. This particular junction setting resembles the molecular film discussed in the main text where D states of the molecules are associated with oxidation whereas A states to reduction, being this situation solely a particular electrochemical setting of Eq. S1. In this case, the analysis will lead to $e^2/C_q = [1/(dn/dE)_l + 1/\text{DOS}_e]$ in which $(dn/dE)_l$ is the density of redox states of the interface in $e^2/C_q = [1/(dn/dE)_l + 1/\text{DOS}_e]$ whereas DOS_e is the DOS of the electrode, which, as noted above, does not contribute to e^2/C_q because it is too high and $1/DOS_e \sim 0$, thus leading to $C_q = e^2 (dn/dE)_l$ for this type of electrochemical interface and junction setting of Eq. S1.

Therefore, in the presence of an electrolyte and for a molecular film attached to an electrode (be it redox-active or not) there will be the possibility of a quantum contribution to the capacitance of the interface besides the still not computed (in Eq. S1) electrostatic contribution. The analysis of both (electrostatic and quantum) contributions requires establishing the concept of electrochemical capacitance C_μ, which brings a well-known (commonly the unique considered) additional energy contribution (electrostatic) besides that associated with molecular chemical states individually coupled to an electrode (and accessible by a time-dependent perturbation of the electrode). In other words, C_μ computes

the addition classical coulombic capacitive contribution besides that of quantum capacitance.

The combination of these two contributions gives rise to the concept of electrochemical capacitance C_μ, which is more appropriate for dealing with electrochemical interfaces comprising quantum molecular moieties attached to an electrode embedded into an electrolytic environment. The contact of a chemically modified electrode with an electrolyte allows the investigation of the electronic structure of individual molecular moieties in the presence of an electrolyte medium, responsible for a key electric-field screening phenomenon [4].

Therefore, the concept of electrochemical capacitance C_μ is an equivalent capacitance that is computed as a result of a series combination of coulombic C_e spatial separation of charge (also referred to as polarization) and quantum C_q capacitive states, as it was defined in Eq. S1, such as that

$$\frac{1}{C_\mu} = \frac{1}{C_e} + \frac{1}{C_q}. \tag{S2}$$

Note that in the classical analysis of two capacitors arranged in series, in which only the coulombic charge separation operates, there is an equivalent amount of charges distributed between the two capacitors and a different electric potential in each of them. However, given the atomic and molecular scales of electrochemical capacitors, one of the capacitances has a different physical origin (unrelated to the Coulomb or Gauss law); however, they can have the same charge and potential difference in the presence of an appropriate electrolyte environment able of screening the charge with consequences that leads to a degeneracy g_e of the electric potential energy, as discussed in the main text.

Worthy to note is that the contribution of C_e must be taken into account for describing the properties of the electrolyte structure within the contributions of the solvent and counter-ions to the quantum electrodynamics associated with C_q. As discussed in the main text, in the presence of an appropriate electrolyte medium, there can be a degeneracy of electrostatic e^2/C_e and quantum e^2/C_q energy states computed as g_e[1] and the total electrochemical energy of the interface can be written in terms of C_q such as $E_\mu = g_e \left(e^2/C_q \right)$.

Accordingly, adding the electrolyte contribution (taken as a degeneracy of g_e) to the dynamics of the quantum rate, the resulting rate is computed as [1]

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[1]Recall, from the main text, that this g_e term refers to an energy degeneracy owing to $C_e \sim C_q$ which is associated with the electric field screening imposed by the electrolyte. It is an additional degeneracy besides the spin degeneracy of the electron g_s. More details on the meaning and origin of g_e as an additional energy degeneracy besides g_s are discussed in the main text.

$$k = \frac{G}{C_\mu} = G_0 \sum_{n=1}^{N} T_n(\mu) \left(\frac{1}{C_e} + \frac{1}{C_q} \right) = g_s g_e \frac{e^2}{hC_q} \sum_{n=1}^{N} T_n(\mu), \quad \text{(S3)}$$

and Eq. S3 is a key first-principle equation that permits us to understand ET and electron transport in its multitude of situations, including long-range electron transport in respiratory chains, as discussed in the main text.

2. THE STATISTICAL MECHANICS OF THE QUANTUM RATE

The zero-temperature approximation of the quantum rate theory is summarized in Eq. S3, corresponding to Eq. 2 of the main text. The consideration of the statistical mechanics and thermal dependence within a finite temperature analysis of Eq. S3 can be conducted simply by rewritten Eq. S3 in the following form

$$k = \frac{G_0}{C_\mu} \sum_{n=1}^{N} T_n(\mu) = g_s \frac{e^2}{hC_\mu} \sum_{n=1}^{N} T_n(\mu) = g_s \frac{E_\mu}{h} \sum_{n=1}^{N} T_n(\mu), \quad \text{(S4)}$$

by noting the meaning of C_μ given by Eq. S2 and $G_0 = g_s e^2/h$. The total electrochemical energy of the system is now recognized as $E_\mu = e^2/C_\mu$, which is not consistent with the thermodynamics owing to it being formulated at the zero-temperature limit. In other words, the temperature dependence required for a room temperature analysis of the electrodynamics involved with the total electrochemical energy is not contained in Eq. S3.

The thermodynamics that corresponds to the thermal dependence of $E_\mu = e^2/C_\mu$ can be quantified using statistical mechanics [1]. Particularly, using the grand canonical ensemble presumption [1], it can be demonstrated that $E_\mu = e^2/C_\mu = (k_B T/N) [f(1-f)]^{-1}$, where $f = (1 + \exp(E/k_B T))^{-1}$ is the Fermi-Dirac distribution function, k_B is the Boltzmann constant, T is the absolute temperature and $E = \mu - E_F$[2]. Therefore, within statistical mechanics considerations, Eq. S4 (or equivalently Eq. S3) can be now rewritten as

$$k = g_e \frac{G}{C_q} = g_e G_0 \left(\frac{k_B T}{e^2 N} \right) [f(1-f)]^{-1} \sum_{n=1}^{N} T_n(\mu). \quad \text{(S5)}$$

which is equivalent to Eq. 9 of the main text if the meaning of g_e is taken into account.

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[2]Note that if there is the consideration of an electrode structure over which there is a molecular system of interest to be studied, it is required a referential energy level. The Fermi level E_F of the junctions is generally taken as the reference level of energy.

3. AMBIPOLAR ELECTRIC CURRENT

Let us now consider an ambipolar diode junction operating at a finite temperature T within an equilibrium potential of E_F/e, where E_F corresponds to the Fermi level of the diode. Accordingly, by definition, at the equilibrium potential E_F/e there is no net current flowing through the diode. However, there is an equilibrium dynamical electric current i_0, which is ambipolar, hence consisting of electron and hole charge carriers, flowing dynamically in the diode.

By applying a very small bias potential V' perturbation over the equilibrium potential E_F/e, that is $V' = V - E_F/e$, it is possible to derive an expression of the conductance for a single charge (electron or hole) transmission through this ambipolar diode. The expression of the conductance is obtained from the $i - V$ curve of the diode which is, considering the i_0 ambipolar electric current[3], defined as

$$i = i_0 \left(\exp\left[\alpha \frac{e}{k_B T} V' \right] - \exp\left[(1 - \alpha) \frac{e}{k_B T} V' \right] \right), \qquad \text{(S6)}$$

which is identical to the Butler-Volmer equation [5, 6], where α corresponds to the transfer coefficient of the diode. Hence, the expression of the conductance is calculated as the derivative di/dV of Eq. S6, which leads, to a transfer coefficient of $1/2$[4], to the conductance quantum defined in terms of i_0 [7]

$$G_0 = \frac{1}{R_q} = \frac{e}{2k_B T} i_0, \qquad \text{(S7)}$$

obtained at the Fermi level of the diode junction, where the term $k_B T/e$ is a constant referred to as the thermal voltage and R_q numerically complies with 12.9 kΩ[5], as demonstrated experimentally in different situation, including the electrochemistry of redox-active molecular junctions [7].

According to the quantum rate theory, the rate ν of charge carriers following in this diode junction at a finite T is defined as $\nu = G/C_q$, where C_q must now be defined in terms of the general definition of capacitance that is given as $1/C = dV/dq$, in which $dq = -edn$. Noting that $d\mu = -edV$, according to the definition of quantum or chemical capacitance provided in section 1, it can be straightforwardly demonstrated that $d\mu/dn = e^2/C_q$ defines the chemical potential difference responsible for the ambivalent equilibrium flowing of charge that gives rise to i_0 of the diode junction, which for a single charge state $dn = 1$ provides

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[3]Observe that this electric current concept applies to both molecular and biological films studied and discussed in the main text

[4]By adopting the transfer coefficient as $1/2$ ($\alpha = 1/2$), it is explicitly taken into account both type of charge carriers (electrons and holes) flowing in the junction.

[5]This is a constant value defined by the expression $h/g_s e^2$, where $g_s = 2$ corresponds to the spin degeneracy of the electron energy state.

the capacitance of a single charge dynamics in a single-channel mode of operation, which leads to $\Delta\mu = e^2/C_q$ for a single quantum channel charging mode of operation of this diode.

Alternatively, note that $d\mu = dE/dn$ also implies a chemical potential difference between D and A states of a $D - A$ system, corresponding to the difference of energy $-eV$ between D and A states. According to, for the diode junction or the i_0 flowing in a $D - A$ system, it can also be demonstrated that

$$C_q = e^2 \left(\frac{dn}{dE} \right), \tag{S8}$$

and hence the quantum or chemical capacitance [1] C_q, for these situations, is directly proportional to the density-of-state (dn/dE) [1, 8, 9]. The simplest way of taking the temperature dependence of C_q defined in Eq. S8 is by considering a Fermi-Dirac occupancy, such as that $f = n/N = (1 + \exp{(E/k_BT)})^{-1}$, from which $dn = Ndf$, where N is the total number of states. Accordingly, Eq. S8 turns into

$$C_q = Ne^2 \left(\frac{df}{dE} \right) = \left(\frac{e^2N}{k_BT} \right) [f(1 - f)], \tag{S9}$$

by noting that $(df/dE) = (1/k_BT) [f(1 - f)]$. At the equilibrium state of energy, i.e., at the Fermi level, $f = 1/2$ and Eq. S9, for a single charge mode of operation for which $N = 1$, turns simply into

$$C_q = \frac{e^2}{4k_BT}. \tag{S10}$$

A thermally dependent $\nu = G_0/C_q$ for a single charge mode of operation can be now defined as the ratio between G_0 stated in Eq. S7 and C_q stated in Eq. S9, such as that

$$\nu = G_0/C_q = 2 \left(\frac{i_0}{e} \right), \tag{S11}$$

which is identical to the result obtained in Eq. 11 or Eq. 12 of the main text. The number 2 in Eq. S11 comes from the fact that although the degeneracy of i_0 was considered in the definition of G_0 provided by Eq. S7, the spin degeneracy of the electron was not (and required as verified experimentally [5]). If the spin degeneracy were considered in the definition of G_0 provided by Eq. S7, Eq. S7 would be formulated as $(e/4k_BT)i_0$ and hence the rate ν would be stated simply as i_0/e, leading to the same result indicated in the main text (see Eq. 12).

REFERENCES

1.   P. R. Bueno, *The Nanoscale Electrochemistry of Molecular Contacts*, SpringerBriefs in Applied Sciences and Technology (Springer, 2018).

2. D. A. Miranda and P. R. Bueno, "Density functional theory and an experimentally-designed energy functional of electron density," Phys. Chem. Chem. Phys. **18**, 25984–25992 (2016).

3. D. A. Miranda and P. R. Bueno, "Chemical hardness of mesoscopic electrochemical systems directly analyzed from experimental data," J. Phys. Chem. C **123**, 21213–21223 (2019).

4. E. F. Pinzon Nieto, E. V. Godoy Alarcon, Y. P. Sanchez, and P. R. Bueno, "Quantum rate dynamics and charge screening at the nanoscale level," Phys. Chem. Chem. Phys. **24**, 16200–16206 (2022).

5. Y. P. Sanchez, A. Santos, and P. R. Bueno, "Quantum mechanical meaning of the charge transfer resistance," J. Phys. Chem. C **126**, 3151–3162 (2022).

6. A. J. Bard and L. R. Faulkner, *Electrochemical Methods Fundamentals and applications* (John Wiley and Sons, 2000), 2nd ed.

7. Y. P. Sanchez, A. Santos, and P. R. Bueno, "Quantum rate efficiency of the charge transfer mediated by quantum capacitive states," Electrochimica Acta **434** (2022).

8. P. R. Bueno and J. J. Davis, "Measuring quantum capacitance in energetically addressable molecular layers," Anal. Chem. **86**, 1337–1341 (2014).

9. S. Luryi, "Quantum capacitance devices," Appl. Phys. Lett. **52**, 501–503 (1988).