Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORT INFORMATION

Capacitance Spectroscopy and Density Functional Theory

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SI. 1. EXPERIMENTAL PROCEDURES AND COMPUTATIONAL METHODS

SI. 1.1. Molecular layer over electrodes

Gold electrodes disks (2.0 mm diameter, Metrohm) were mechanically polished with aluminum oxide pads or diamond spray on polishing cloth (Kemet) of progressively decreasing particle size: 1 µm, 0.3 µm and 0.05 µm, with intermittent sonication in water. The electrodes were then electrochemically polished in a deaerated NaOH or KOH 0.5 mol L^{-1} between the potentials -1.5 V and -0.5 V vs. Ag|AgCl or Ag wire at a scan rate of 100 mV s^{-1} and then in deaerated 0.5 M H_2SO_4 between -0.2 V and 1.5 V at 100 mV s^{-1} until stabilization of the gold reduction peak (around 50 cycles). Electroactive areas were evaluated by integration of the cathodic peak from gold electropolishing voltammograms and converted to the real surface area using a conversion factor of 400 µC cm^{-2}. These determinations of area 0.033-0036 cm^2 and the thickness (estimated herein as 0.80-085 nm) were used in the normalization of absolute recorded capacitance per area.

Electro active Self-Assembled Monolayers (SAMs) were prepared by immersion of the gold electrodes (AUTOLAB) in 6-ferrocenyl-hexanethiol (Sigma Aldrich) (1:100).[1-4] Electrodes prepared according to the above procedure were finally used as working electrode for CS measurements. Electrochemical experimental measurements were done in triplicate and 6-ferrocenyl-hexanethiol was the experimental system elected to be directly compared with computational DFT atomistic simulation according to the main text.

SI. 1.2. Capacitance Spectroscopy Measurements

All electrochemical measurements were undertaken on a Autolab PGSTAT fitted with an FRA2 module. A three electrode cell setup was used with a gold (BASi) working electrode, a platinum wire auxiliary electrode and a Ag|AgCl as reference electrode. Impedance spectra were collected between 1 MHz and 0.01 Hz with amplitude of 10 mV (peak to peak) and were subsequently verified for compliance with linear systems theory by Kramers–Kronig by employing the FRA AUTOLAB software. The redox capacitive nature of these interfaces can be sensitively analysed measuring complex $Z^{*}(\omega)$ (impedance) function and conversion into $C^{*}(\omega)$ (capacitance) by $C^{*}(\omega) = 1/i\omega Z^{*}(\omega)$, where ω is the angular frequency and $i = \sqrt{-1}$ (i.e., complex number). Practically, this involves taking the data resolved in a standard impedance analysis ($Z^{*}(\omega)$), sampled across a range of frequencies at any steady-state potential, and converting it phasorially into complex capacitance ($C^{*}(\omega)$) with its real and imaginary components. In processing $Z^{*}(\omega)$ datasets in this way one obtains the imaginary part of the capacitance by noting that $C'' = \varphi Z'$ and real part that $C' = \varphi Z''$, where $\varphi = (\omega|Z|^{2})^{-1}$ and $|Z|$ is the modulus of Z^{*}. If one carries out this analysis outside of the surface potential window where redox activity is observed and then inside the potential window, the difference (the "redox only capacitive term", C_r) is obtained.[1, 4] It should be noted that, in the absence of a redox film, charging capacitance is comparatively very small for higher molecular coverage, C_r can, alternatively, be estimated by simple subtraction of the former.[1, 4] However, without this condition it is recommended that acquisition of capacitance data in and out of the redox potential window for all interfaces is an appropriate pre-requisite (the procedures is detailed indicated in previous works[1-4] and summarized in Figure 7 of the main text).

SI. 1.3. Computational Methods

The different contributions to the energy and capacitance are calculated using the deduced formulas as indicated in SI. section 3 and Eqn. (18) of the main text with the aid of the SIESTA software[5] DFT code. The prototype system consists of a gold cluster in which ferroceny-hexanethiol (representing a well-characterised and commonly used redox probe) is covalently attached (unprotonated) in a gold slab in the Au(100) configuration and inserted in a box of 28.837 x 28.837 x 54.736 Å with angles of $\alpha = 90$ and $\beta = 120$ degrees [as shown in Figure 4]. This system was compared with isolated ferroceny-hexanethiol (the protonated form of the thiol). The latter has 40 atoms and is coupled to a gold metal slab of 300 atoms to form the prototype system that represents the mesoscopic system of interest in the present study to be evaluated from DFT atomistic point of view. The alkylferrocene moiety is oriented with its principal axis of inertia aligned with the z-axis. The DFT electronic energy calculations (see Table 1 of main manuscript) are performed for both the isolated ferrocenyl-hexanethiol molecule and the metal-molecule system at a fixed geometry optimized using the DFT code geometry optimization algorithms which minimize the potential energy of the system. The convergence criteria used was that the forces in the atoms are smaller than 0.05 eV $Å^{-1}$.

For the description of the DFT electronic wave functions [Kohn-Sham (KS) equations], as in any quantum mechanics methodology[6], the general solution of the problem is searched by expanding the general wave function into equations by a linear combination of atom-centered atomic orbitals, and the mathematical functions chosen to describe these orbitals are spherical harmonics functions, expressed in spherical coordinates. For the radial two mathematical functions are assigned per atom's angular momentum (so called double zeta function), and for the angular dependence, one extra mathematical function is added for higher angular momentum orbitals (so called polarization function). In summary, a numerical double-zeta-polarized (DZP) basis function[7] was employed to numerically solve the KS equations. The KS equations are also a function of the real coordinate space, and this space is discretized, in the particular DFT implementation used in this work, which generates a 3D grid of points where the KS equations are expressed. The fineness of this grid is controlled by the maximum kinetic energy that a wave can achieve, which defines its wavelength (hence, it defines the spacing of the grid). This energy cutoff was chosen to be 250 Ry in all calculations (which gives the precision of the calculation as shown in Tables 1 of the main text).[2] In order to achieve further decrease in computational effort, the number of explicit electrons is reduced by replacing the effect of the core electrons over the valence electrons, by the effective potential exerted by the core on the valence electrons. This partition generates an ionic core region (the nucleus plus core electrons) and the explicitly treated valence electrons. The potential of this ionic core is also referred to as "pseudo-potential", and it is obtained, for each different chemical element, by solving the DFT Schröedinger equation for the corresponding isolated atom and numerically inverting the equation, to obtain the potential from the wave functions.[8, 9] There are many methodologies to construct this pseudo-potential, and specifically in this work we employed the Troullier-Martins methods of pseudo-potentials.[9] For the description of the electronic exchange interaction and electron correlation, the Generalized Gradient Approximation (GGA) is employed, under the Perdew-Burke-Ernzerhof (PBE) implementation, through the GGA-PBE exchange-correlation functional.[10] Herein besides PBE and BLYP functionals of the SIESTA software code[5] calculations were made using O3LYP and B3LYP of the ORCA software code[11] in smaller model compounds of gold nanoclusters attached to ferrocene-alkanethiol. This produced comparable results to those of the SIESTA in order to be aware of the relative energy provided by different functionals.

SI. 1.4. Quantum Capacitance of an N-electron system

When a battery (external potential or driven force) is connected to a classical parallel-plate capacitor (see Figure 2*a*), charge flows from one side of the plate to the other, and the flow stops when the external potential of the battery equates. Hence, the source of the energy variation is purely electrostatic. In case of the potential difference between a metallic plate and an N-electron charged system (see Figure 2*b*), there are many electronic states that lie over the same level (the Fermi level) in the metallic plate and the electronic energy per electron (the chemical potential) is rigidly shifted by the external potential in the coupled N-electron system as a consequence that states are limited on this part of the junction. In other words, when one of the plates (the N-electron system for instance) has a limited number of electronic states (like a confined system, as the case of redox SAMs in gold) the electronic transfer cannot happen at any energy, and each electron transferred changes the energy of the other electrons already present in the system, that is, it shifts the local chemical potential considerably for a mesoscopic capacitor,[12] where the density of states is usually small. Therefore, a correction term must be included in the electrostatic capacitance, to correctly account for this effect. This correction is the quantum capacitance, defined in 1988 by Serge Luryi.[13] The expression for this quantum capacitance is defined, in the original reference,[13] for the two dimensional electron gas model, and the definition leads to the equation $C_q = e^2 g_r(E_F)$, where $g_r(E_F)$ is the density of states of the system at the Fermi level. However, in molecular systems, the density of states at the Fermi level itself cannot be defined. There is, however, a definition for the quantum capacitance for a molecule, which is deduced below (SI. section 3), in the context of the DFT. The final result is $C_q = e^2 / (\varepsilon_{N+1} - \varepsilon_N)$, or more commonly, $\varepsilon_{N+1} - \varepsilon_N = e^2 / C_q$, where $\varepsilon_{N+1} - \varepsilon_N$ is just given by the difference between HOMO and LUMO orbital energies. Indeed, $1/(\varepsilon_{N+1} - \varepsilon_N)$ behave like $g_r(E)$ when metallic states energies are aligned with those of molecular orbitals states of redox active centres and thermal broadening is taken into account as demonstrated in the main text (see the junction of Figure 2*b* and the corresponding calculated electronic structure shown in Figure 6*b*).

The DFT calculation supplies orbital energies, among many other parameters and properties, in a typical DFT quantum mechanical calculation, but not the density of states (DOS) itself. The DOS is usually obtained by the convolution of the orbital energies spectrum combined with broadening mathematical function (Lorentz-Boltzmann statistics) that simulates experimental uncertainties such as, for instance, thermal fluctuations. The latter procedure turns the discrete spectrum into a continuous function.

Indeed, the quantum capacitance in molecular junctions depends, in the particular chemical system studied herein, on the ferrocene attachment to the gold. This attachment change the molecular states (orbitals) wave functions and a new pattern of frontier orbitals configuration arises with contributions from the gold atomic orbitals on the ferrocene molecular system, specifically affecting the iron atomic orbitals.

Even though there are known concerns, regarding the relationship of KS eigenvalues with physical observables, especially when employing pure exchange-correlation functionals, this relationship of the KS eigenvalues to quantum contributions on energy variation upon charging is well established.[5]

Although in the main text, the qualitative comparison and analysis were made always among simple cluster model systems, a final calculation was made with molecular ferrocene films in the metallic surface, to check for quantitative agreement. In this calculation, 25 alkylferrocene molecules were used as the SAM representative structure (the maximum coverage possible, in the geometry chosen for the metal slab). In this case, since the spacing of the levels is even smaller, the spectrum was broadened with a Gaussian function of width 0.01 eV. The results indicate a density of states of 120 states eV^{-1} at the Fermi level, relative to the pure gold calculation. When applying $C_q = e^2 g_r(E_F)$ it results in a capacitance of ~19 *a*F. Since the area of the SAM-metal corresponding to the electrode is ~830 Å^2, it leads to a surface capacitance of ~230 μF cm^{-2}. This calculation was made without any solvent or support electrolyte but even though compares very well with CS results in low polarity solvents (see Figure 7*a* and 7*b*).

SI. 2. SOME KEY FUNDAMENTS OF DENSITY FUNCTIONAL THEORY

The deduction of the expressions used for the calculation of capacitance for molecular systems were made herein leading to equivalent results obtained by Luo *et. al.*[14] In light of the DFT theory, the system Hamiltonian is written as a functional of the electron density

$$E[\rho(\vec{r})] = T_0[\rho(\vec{r})] + \int_\Omega \rho(\vec{r})v(\vec{r})d\vec{r} + \frac{1}{2}\iint_{\Omega\times\Omega} \frac{e^2\rho(\vec{r})\rho(\vec{r}\,')}{4\pi\varepsilon_0|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,' + E_{xc}[\rho(\vec{r})] + V_{nn}$$

(SI. 1)

where $\rho(\vec{r}) = \sum_i^N \psi_i^* \psi_i$ is the electron density of the system, written here in terms of the system's wavefunction. Ω in the integrands represents the spatial region where the N-electron system is stated. T_0 is the kinetic energy of the system of a ficticious system of non-interacting electrons, the second and third terms are the interaction energy of the electrons with an external potential and the electron-electron Coulomb energy, respectively. E_{xc} is the exchange-correlation term and V_{nn} is the internuclear Coulomb interaction energy. In the particular case where the external potential is the Coulomb potential created by the nuclei $v(\vec{r}) = \sum_a \frac{Z_a e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_a|}$, the energy expression becomes

$$E[\rho(\vec{r})]=T_0[\rho(\vec{r})]+\sum_a\left[\int_\Omega \frac{Z_a e^2\rho(\vec{r})}{4\pi\varepsilon_0|\vec{r}-\vec{R}_a|}d\vec{r}\right]+\frac{1}{2}\iint_{\Omega\times\Omega}\frac{e^2\rho(\vec{r})\rho(\vec{r}')}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'+E_{xc}[\rho(\vec{r})]+V_{nn} \quad \text{(SI. 2)}$$

Minimization of this functional by the variational method, under the constrain that the number of electrons N is constant (that is, $N=\int_\Omega \rho(\vec{r})d\vec{r}$) is carried out using the Lagrange multipliers method

$$\frac{\delta E[\rho(\vec{r})]}{\delta\rho(\vec{r})}-\varepsilon\left\{\frac{\delta}{\delta\rho(\vec{r})}\left(\int_\Omega \rho(\vec{r})d\vec{r}-N\right)\right\}=0 \quad \text{(SI. 3)}$$

where ε is the Lagrange multiplier. This leads to the following equation

$$\int_\Omega \delta\rho(\vec{r})\left\{\frac{\delta T_0[\rho(\vec{r})]}{\delta\rho(\vec{r})}+\sum_a\frac{Z_a e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_a|}+\int_\Omega\frac{e^2\rho(\vec{r}')}{4\pi\varepsilon_0|\vec{r}-\vec{r}'|}d\vec{r}'+\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}-\varepsilon\right\}d\vec{r}=0 \quad \text{(SI. 4)}$$

where the answer is obtained by imposing the sum of the terms in the brackets to be zero. The only known expression for the kinetic energy is given in terms of the wavefunction as: $T_0=-\frac{\hbar^2}{2m}\sum_i^N\int_\Omega \psi_i^*(\vec{r})\nabla^2\psi_i(\vec{r})d\vec{r}$, so the derivatives must be taken relative to the wavefunction, rather than the density. Taking the derivatives of this expression using the chain rule, we arrive at the Kohn-Sham (KS) equations[15, 16]

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r})+V_{ef}(\vec{r})\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r}) \quad \text{(SI. 5)}$$

where each ε_i for i = 1,2, … N are the values of each Lagrange multiplier, interpreted as the KS orbital energies, and V_{ef} is the Kohn-Sham effective potential, given by

$$V_{ef}=\frac{e^2}{4\pi\varepsilon_0}\sum_a\frac{Z_a}{|\vec{r}-\vec{R}_a|}+\frac{e^2}{4\pi\varepsilon_0}\int_\Omega\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'+\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \quad \text{(SI. 6)}$$

and the quantity $H_{KS}=\frac{-\hbar^2}{2m}\nabla^2+V_{ef}(\vec{r})$ is the full KS Hamiltonian. The KS equations are, in summary, one-particle Schröedinger equations, and the KS orbital energies are obtained as eigenvalues ε_i of the KS Hamiltonian.

SI. 3. THE CAPACITANCE OF AN N-ELECTRON SYSTEM IN DENSITY FUNCTION THEORY

The following deduction comes from the work of Luo et al[3]. Suppose that we want to calculate the capacitance of a system that gets charged, that is, the total number of electrons change from N to

$N' = N + dN$. Naming $\rho'(\vec{r})$ the electron density of the charged system, the equation for the effective KS potential can be written as

$$V'_{ef} = \frac{e^2}{4\pi\varepsilon_0}\sum_a \frac{Z_a}{\left|\vec{r}-\vec{R}_a\right|} + \frac{e^2}{4\pi\varepsilon_0}\int_\Omega \frac{\rho'(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}' + \frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})} \tag{SI. 7}$$

If we assume that the geometry of the charged system does not change appreciably, with respect to the neutral species, the difference between the KS potentials will be another constant, and can be written as

$$V'_{ef} - V_{ef} = \frac{e^2}{4\pi\varepsilon_0}\left\{\int_\Omega \frac{\rho'(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}' - \int_\Omega \frac{\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}'\right\} + \left\{\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})} - \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right\} \tag{SI. 8}$$

In classical electromagnetism, the electrostatic potential of a given charge distribution $\rho(\vec{r})$ is expressed as $V = \frac{1}{4\pi\varepsilon_0}\int_\Omega \frac{\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}'$, and it can be related directly to the capacitance

$$\frac{e^2}{4\pi\varepsilon_0}\left\{\int_\Omega \frac{\rho'(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}' - \int_\Omega \frac{\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}'\right\} = \frac{(N'-N)e^2}{C} \tag{SI. 9}$$

which has a sense of a “classical” (or electrostatic) capacitance, indeed due to its origin.

Assuming that the variations in the density are not sharp during the charging process, since the exchange-correlation potential is dependent on the gradient of the density, we can also write

$$V'_{ef} - V_{ef} = \frac{(N'-N)e^2}{C} \tag{SI. 10}$$

Since the difference is a constant, due to the structure of the KS Hamiltonian, the KS eigenvalues will be shifted rigidly by the same amount

$$\varepsilon'_i - \varepsilon_i = \frac{(N'-N)e^2}{C} \tag{SI. 11}$$

In order to clarify the classical and quantum contributions to the capacitance, the total energy of the system can then be rewritten in terms of the KS eigenvalues as

$$E[\rho(\vec{r})] = \sum_i^N \varepsilon_i^{KS} - \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\iint_{\Omega\times\Omega} \frac{\rho(\vec{r})\rho(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}d\vec{r}' + E_{xc}[\rho(\vec{r})] - \int_\Omega \rho(\vec{r})\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}d\vec{r} + V_{nn} \tag{SI. 12}$$

Suppose that we want to calculate the capacitance of a system that gets charged, that is, the total number of electrons change from N to N'. Remembering the electron density of the charged system was named previously as $\rho'(\vec{r})$, the equation for the total energy can be stated as

$$E[\rho'(\vec{r})]=\sum_{i}^{N'}\varepsilon_i'^{KS}-\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\iint_{\Omega\times\Omega}\frac{\rho'(\vec{r})\rho'(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'+E_{xc}[\rho'(\vec{r})]-\int_{\Omega}\rho'(\vec{r})\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}d\vec{r}+V_{nn} \tag{SI. 13}$$

and hence, the total energy change is

$$\begin{aligned}E[\rho'(\vec{r})]-E[\rho(\vec{r})]&=\left(\sum_{i}^{N'}\varepsilon_i'^{KS}-\sum_{i}^{N}\varepsilon_i^{KS}\right)-\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\left(\iint_{\Omega\times\Omega}\frac{\rho'(\vec{r})\rho'(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'-\iint_{\Omega\times\Omega}\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'\right)\\&+\left(E_{xc}[\rho'(\vec{r})]-E_{xc}[\rho(\vec{r})]\right)-\left(\int_{\Omega}\rho'(\vec{r})\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}d\vec{r}-\int_{\Omega}\rho(\vec{r})\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}d\vec{r}\right)\end{aligned} \tag{SI. 14}$$

In order to eliminate the explicit dependence of this expression with the coulomb and exchange-correlation terms, we need to use the equations from the effective KS potential. From Eqn. (SI. 8) and (SI. 10) we have

$$\frac{e^2}{4\pi\varepsilon_0}\left\{\int_{\Omega}\frac{\rho'(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'-\int_{\Omega}\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'\right\}+\left\{\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right\}=\frac{(N'-N)e^2}{C} \tag{SI. 15}$$

If we multiply Eqn. (SI. 15) by $\rho(\vec{r})/2$ and integrate over $\vec{r}$, we get

$$\begin{aligned}&\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\iint_{\Omega\times\Omega}\frac{[\rho'(\vec{r}')-\rho(\vec{r}')]\rho(\vec{r})}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'+\frac{1}{2}\int_{\Omega}\rho(\vec{r})\left(\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)d\vec{r}\\&=\frac{1}{2}\int_{\Omega}\rho(\vec{r})\frac{(N'-N)e^2}{C}d\vec{r}=\frac{1}{2}\frac{N(N'-N)e^2}{C}\end{aligned} \tag{SI. 16}$$

Likewise, if we multiply Eqn. (SI. 15) by $\rho'(\vec{r})/2$ and integrate over $\vec{r}$, we get

$$\begin{aligned}&\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\iint_{\Omega\times\Omega}\frac{[\rho'(\vec{r}')-\rho(\vec{r}')]\rho'(\vec{r})}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'+\frac{1}{2}\int_{\Omega}\rho'(\vec{r})\left(\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)d\vec{r}\\&=\frac{1}{2}\int_{\Omega}\rho'(\vec{r})\frac{(N'-N)e^2}{C}d\vec{r}=\frac{1}{2}\frac{N'(N'-N)e^2}{C}\end{aligned} \tag{SI. 17}$$

Summing the Eqns. (SI. 16) and (SI. 17), we get

$$\begin{aligned}&\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\iint_{\Omega\times\Omega}\frac{\rho'(\vec{r})\rho'(\vec{r})}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2}\iint_{\Omega\times\Omega}\frac{\rho(\vec{r}')\rho(\vec{r})}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}'\\&=-\frac{1}{2}\int_{\Omega}[\rho(\vec{r})+\rho'(\vec{r})]\left(\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)d\vec{r}+\frac{1}{2}\frac{\left(N'^2-N^2\right)e^2}{C}\end{aligned} \tag{SI. 18}$$

Substituting this result in Eqn. (SI. 14)

$$\begin{aligned}E[\rho'(\vec{r})]-E[\rho(\vec{r})]&=\left(\sum_{i}^{N'}\varepsilon'^{KS}_{i}-\sum_{i}^{N}\varepsilon_{i}^{KS}\right)\\&+\frac{1}{2}\int_{\Omega}[\rho(\vec{r})+\rho'(\vec{r})]\left(\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)d\vec{r}-\frac{1}{2}\frac{\left(N'^{2}-N^{2}\right)e^{2}}{C}\\&+\left(E_{xc}[\rho(\vec{r})]-E_{xc}[\rho(\vec{r})]\right)-\left(\int_{\Omega}\rho'(\vec{r})\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}d\vec{r}-\int_{\Omega}\rho(\vec{r})\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}d\vec{r}\right)\end{aligned} \qquad \text{(SI. 19)}$$

We can also rearrange Eqn. (SI. 11) involving the KS eigenvalues to get

$$\sum_{i}^{N'}\varepsilon_{i}'^{KS}-\sum_{i}^{N}\varepsilon_{i}^{KS}=\sum_{i}^{N'}\left[\varepsilon_{i}^{KS}+\frac{(N'-N)e^{2}}{C}\right]-\sum_{i}^{N}\varepsilon_{i}^{KS}=\sum_{N+1}^{N'}\varepsilon_{i}^{KS}+\frac{N'(N'-N)e^{2}}{C} \qquad \text{(SI. 20)}$$

and substitute in the first term of the right side of Eqn. (SI. 19)

$$\begin{aligned}E[\rho'(\vec{r})]-E[\rho(\vec{r})]&=\sum_{N+1}^{N'}\varepsilon_{i}^{KS}+\frac{N'(N'-N)e^{2}}{C}\\&+\frac{1}{2}\int_{\Omega}[\rho(\vec{r})+\rho'(\vec{r})]\left(\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}-\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\right)d\vec{r}-\frac{1}{2}\frac{\left(N'^{2}-N^{2}\right)e^{2}}{C}\\&+\left(E_{xc}[\rho'(\vec{r})]-E_{xc}[\rho(\vec{r})]\right)-\left(\int_{\Omega}\rho'(\vec{r})\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}d\vec{r}-\int_{\Omega}\rho(\vec{r})\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}d\vec{r}\right)\end{aligned} \qquad \text{(SI. 21)}$$

To completely eliminate the exchange-correlation terms, we can use the approximation

$$\left(E_{xc}[\rho'(\vec{r})]-E_{xc}[\rho(\vec{r})]\right)=\int_{\Omega}[\rho'(\vec{r})-\rho(\vec{r})]\frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}d\vec{r}=\int_{\Omega}[\rho(\vec{r})-\rho'(\vec{r})]\frac{\delta E_{xc}[\rho'(\vec{r})]}{\delta\rho'(\vec{r})}d\vec{r} \qquad \text{(SI. 22)}$$

This holds whenever the variation in density is small, and usually happens to be the case of large systems/molecules. Finally, upon substitution of Eqn. (SI. 22) into Eqn. (SI. 21), the following expression is obtained

$$E(N')-E(N)=\sum_{N+1}^{N'}\varepsilon_{i}^{KS}+\frac{(N'-N)^{2}e^{2}}{2C} \qquad \text{(SI. 23)}$$

Applying this equation to the particular case where $dN=\pm 1$, i.e. for $N'=N+1$ or $N'=N-1$, an even simpler form is obtained:

$$E(N+1)-2E(N)+E(N-1)=\varepsilon_{N+1}-\varepsilon_{N}+\frac{e^{2}}{C} \qquad \text{(SI. 24)}$$

The more general definition of the capacitance as electrochemical (or redox) capacitance, equivalently to Eqn. 14 of the main text, follows

$$\frac{e^2}{C_r(N)} = \mu(N+1) - \mu(N) = E(N+1) - 2E(N) + E(N-1) \qquad \text{(SI. 25)}$$

As a more general definition this expression does not explicitly shows the contribution of the quantum levels to variations in energy between charged and neutral systems. One can think of $C_r(N)$ as the total capacitive contribution (within electrostatic and quantum terms), which is actually measured experimentally by capacitance spectroscopy approach (see main text). Indeed it can be clarified that the right-hand side of Eqn. (SI. 24), is indeed the classical Coulomb contribution and is clearly separated from the quantum correction capacitive contribution, in so observing (by comparing Eqn. SI. 24 and SI. 25) the following expression can be written

$$\frac{e^2}{C_r(N)} = \frac{e^2}{C_q} + \frac{e^2}{C_e}, \qquad \text{(SI. 26)}$$

where finally the correspondence with quantum density functional theory is established

$$\varepsilon_{N+1} - \varepsilon_N = \frac{e^2}{C_q} \qquad \text{(SI. 27)}$$

In summary, the Eqn. (SI. 26) is equivalent to $1/C_r = 1/C_e + 1/C_q$ (according to the equivalent circuit of Figure 1*e* of the main text). Although Eqn. (SI. 26) was previously introduced by us in the context of capacitance spectroscopy analysis, the correspondence of this general capacitive analysis with DFT theory was not previously stated so that constituting the main goal of the present work.

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