

Capacitive nature of atomic-sized structures

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The capacitance of an N -electron system is established by deriving the atomistic connection between the capacitive energy, the ionization potential, and the electron affinity of the charged system; it is shown further that this connection leads to the linkage of the capacitive energy to the difference between the lowest unoccupied and the highest occupied Kohn-Sham orbital energies of the system. An illustrative example is used to show explicitly the microscopic behavior of the derived capacitance for a finite electron system, and to discuss the tendency of the derived capacitance to limit toward the classical electrostatic capacitance as the system becomes macroscopically large. Discussions relevant to atomic and molecular systems are included.

As semiconductor technology continues to drive the scaling of electronic device dimensions into the ultrasub-micrometer, nanodimensional regime, many new physical concepts and atomistic phenomena will continue to be put forth for notional consideration and exploitation. The stunning achievements of nanofabrication technology in the past decade now allow for band engineering and atomic-level structural tailoring not heretofore available or explorable, except through naturally occurring atomic and molecular processes. Nanofabrication tools make possible experimental studies of nanosize electronic structures with capacitance levels in the attofarad region and measurable currents resulting from the controllable passage of a single electron. Therefore, it is timely to consider the capacitive nature of atomic-size structures.

In this paper, the capacitance of an N -electron system is established by deriving the atomistic connection between the capacitive energy, the ionization potential, and electron affinity of the charged system; this connection leads to the further linkage of capacitive energy to the difference between the lowest unoccupied and the highest occupied Kohn-Sham orbital energies of the system. An illustrative example is used to discuss the behavior of the derived capacitance for a finite number of electrons, and to discuss the tendency of the capacitance to approach the classical electrostatic limit as the system becomes macroscopically large, that is, as the number of electrons, " N ," gets large. Extended discussions relevant to atomic and molecular systems are also included.

The differential capacitance, C , of a charged system (hereafter referred to as simply capacitance) determines the specific amount of work per unit charge, ΔV , required to bring a fixed amount of charge, ΔQ , from the vacuum

level to the system in question. As such,

$$\frac{1}{C} \equiv \frac{\Delta V}{\Delta Q} . \quad (1)$$

Macroscopically, capacitance is a system-specific quantity; it is dictated by the materiel characteristics of the system. Conventionally, ΔV and ΔQ are established from Maxwell's equations of classical electrostatics, and when used in Eq. (1), lead to the familiar result that capacitance is independent of the amount of charge added to the system and depends only on the geometrical parameters of the system as well as the static dielectric constant, if insulators are present. For a conducting circular dot of radius R , filled with material having relative dielectric permittivity ϵ_r , the resulting classical capacitance is $C = 8\epsilon_0\epsilon_r R$.

From an atomistic viewpoint, the capacitance of the system is determined by using for ΔV ,

$$e\Delta V = \mu(N + \Delta N) - \mu(N) \equiv \Delta\mu , \quad (2)$$

where $\mu(N)$ is the chemical potential of an N -particle system; then, using $\Delta Q = e\Delta N$ with $\Delta N = 1$ for a single electron, the capacitance from Eq. (1) can be written¹ as

$$\frac{e^2}{C(N)} = \mu(N + 1) - \mu(N) . \quad (3)$$

Here, it is noted that C is considered to be a function of N , the total number of electrons in the system, because $\mu(N)$ is not typically a linear function of " N " for all N .

The chemical potential for an N -particle system^{2,3} is

$$\mu(N) = E(N) - E(N - 1) , \quad (4)$$

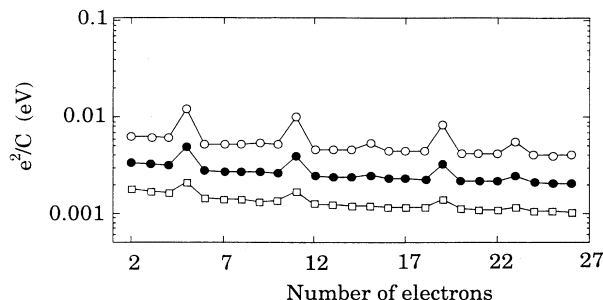


FIG. 1. Capacitive energy vs electron number for a GaAs quantum dot with a radius of 200 nm (empty squares), 100 nm (solid circles), and 50 nm (empty circles).

where $E(N)$ is the total energy of the N -particle system; it is further noted² that

$$I(N) = E(N-1) - E(N) \quad (5)$$

and

$$A(N) = E(N) - E(N+1) \quad (6)$$

are the ionization potential and the electron affinity of an N -particle system. Therefore, the capacitance of Eq. (7) can be written as

$$\frac{e^2}{C(N)} = I(N) - A(N). \quad (7)$$

The identification of the atomistic connection, as expressed in Eq. (7), between the capacitive energy of the system and the quantum-mechanical ionization potential and electron affinity is the central result of this communication.

There are some interesting points to be made concerning the result of Eq. (7). First, the quantity $I-A$ has long been considered by the chemistry community³ as “absolute hardness” of electron transfer denoted by

$$\eta = \frac{1}{2}(I - A), \quad (8)$$

and is used in conjunction with

$$\chi = \frac{1}{2}(I + A), \quad (9)$$

the electronegativity³ of the N -particle system, to address chemical bonding and reaction processes. The quantity “absolute hardness” as noted in Eq. (8) can be identified through the use of Eq. (7), as

$$\eta = \frac{1}{2}(I - A) \equiv \frac{1}{2} \frac{e^2}{C(N)}; \quad (10)$$

thus, η is simply the Coulomb blockade⁴ threshold energy, the minimum capacitive energy to be overcome in adding one electron to an N -particle system. In fact, from Eqs. (9), (10), it follows that

$$I(N) = \chi(N) + \frac{1}{2} \frac{e^2}{C(N)}, \quad (11)$$

and

$$A(N) = \chi(N) - \frac{1}{2} \frac{e^2}{C(N)}, \quad (12)$$

further indicating that the Coulomb-blockade energy is the minimum capacitive energy required to remove or add a single electron to an N -particle system.

Second, density-function theory (DFT) reveals² that

$$I(N) - A(N) = \epsilon^{\text{LU}}(N) - \epsilon^{\text{HO}}(N) + B_0, \quad (13)$$

where $\epsilon^{\text{LU}}(N)$ and $\epsilon^{\text{HO}}(N)$ are the lowest unoccupied and the highest occupied Kohn-Sham orbital energies, respectively, for an N -particle system, and B_0 is nearly a constant. Therefore, the capacitance defined from Eq. (7) can be written in quantum-mechanical terms as

$$\frac{e^2}{C(N)} = \epsilon^{\text{LU}}(N) - \epsilon^{\text{HO}}(N) + B_0. \quad (14)$$

From this expression, the atomistic features of the capacitance are easily understood. As noted in Fig. 1, recent DFT calculations of e^2/C for individual GaAs quantum dots⁵ of various radii show a remarkable structure; the dramatic jump in e^2/C occurs for values of N which begin the filling of the next atomic shell of the quantum-confined system. For the quantum dot system under consideration, the energy levels of the subshell orbital states are almost equally spaced so that the right-hand side of Eq. (14) is nearly constant until the next lowest unoccupied orbital state available for filling is in the next shell, in which case a jump occurs in e^2/C upon filling. The quantity $I-A$ has also been calculated⁶ for jellium spheres and clusters; indeed, the jump characteristics similar to those shown in Fig. 1 are reported. In general, it is noted that when the symmetry of the potential in question results in subshells with accidental degeneracy, then the difference between the lowest unoccupied and highest occupied orbital energies within the subshells will be zero; in this case, a structure similar to that of Fig. 1 will appear for the capacitance of the system.

Third, it is interesting to examine the behavior of e^2/C as N gets very large. Figure 2 depicts the charge-density profile variation with increasing “ N ” for the quantum-dot system of radius 100 nm described in Fig. 1; as N approaches thirty, the electron density begins to uniformly conform to the geometry of the dot and the capacitance tends to the classical electrostatic limit (for GaAs dots, $\epsilon_r = 12.9$; with $R = 100$ nm, $C = 8\epsilon_0\epsilon_r R \approx 0.09$ fF and $e^2/C \approx 0.002$ eV). In going to the limit of macroscopic systems, i.e., as “ N ” gets very large, $[\epsilon^{\text{LU}}(N) - \epsilon^{\text{HO}}(N)]$ tends toward zero, so that B_0 tends to e^2/C (classical) in the large- N limit; this tendency is clearly evidenced in the work of Perdew⁶ on jellium spheres.

The implications inherent in Eq. (7) are significant from several interdisciplinary viewpoints. First, there are many concepts and experiments being put forth today, which utilize atomic-sized nanostructures;⁷ quantum-wells,⁸ quantum-confining dots,⁵ tunneling tips⁹ formed by clusters of atoms, are just a few examples of where a microscopic view of quantum capacitance is not only essential for understanding the charge-transfer dynamics,

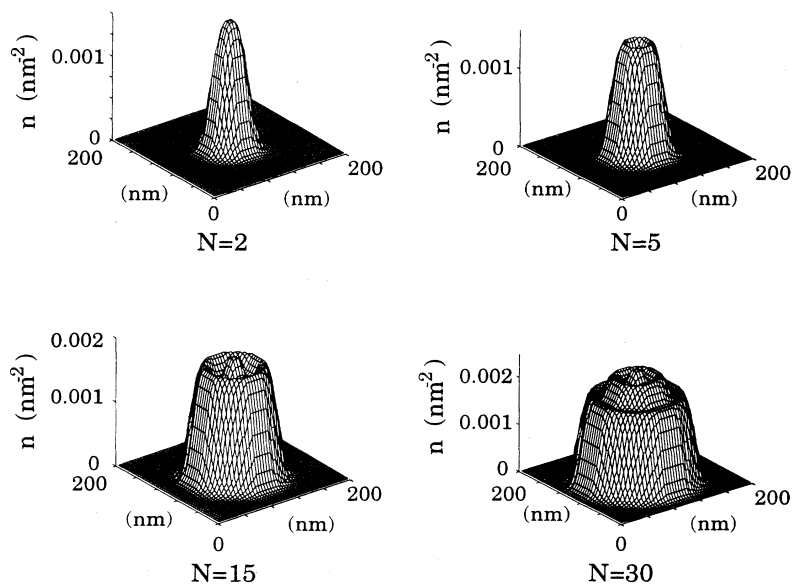


FIG. 2. Electron-density profiles corresponding to electron numbers 2, 5, 15, and 30 for a GaAs quantum dot with a radius of 100 nm (see Fig. 1, solid circles, for corresponding capacitance energy versus electron number analysis).

but is also a way to probe many-body effects in such structures. Second, the concept of quantum capacitance as applied to molecular bonding is different, and may provide an appealing reference frame for further development of principles of bonding theory as originally conceived by Pauling¹⁰ and Mulliken.¹¹ Quantum capacitance in coupled atomic systems will be a topic of future research.

Last, it is evident that the quantum concept of capacitance is fundamental to charge dynamics in electronics as well as atomic and molecular science. Moreover, the powerful method of density-functional theory provides the underpinning by which key many-body characteristics can be taken into account in atomic-sized structures and allows for realistic, user friendly simulations to be performed on complex physical and chemical systems.

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