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Quantum capacitances of molecules, fullerenes and carbon nanotubes by the partitioned real-space density functional method

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Abstract. Capacitances of molecules, fullerenes and carbon nanotubes under the condition of no electron-tunneling are calculated by the partitioned real-space density functional method that has been recently developed. We found that a quantum capacitance of a spherical jellium bielectrode decreases and approaches the classical value as the electron density increases. The capacitances of fullerenes and carbon nanotubes do not depend on the detailed atomic geometry but on the overall shapes. The values of the capacitances of these nanostructures are found to be a few 10^{-20} F and are compatible with the experimental ones determined by the scanning tunneling microscopy studies.

PACS. 31.15.Ar Ab initio calculations – 31.15.-p Calculations and mathematical techniques in atomic and molecular physics (excluding electron correlation calculations) – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Capacitance plays a very important role in many nanoscale physical phenomena such as Coulomb blockade (CB) and nanosized device applications. In particular, CB phenomena which occur in nanosized junctions at low temperatures is essentially characterized by the capacitance of the junction [1]. In the scanning capacitance microscopy (SCM) experiment, capacitance between the SCM tip and the sample surface is measured to investigate the electronic properties of semiconductor surfaces [2].

Recently, capacitances of a gold cluster with 5 nm size [3] and a cyclopentene molecule [4] have been obtained from the current-voltage characteristics in the scanning tunneling microscopy (STM) studies. The capacitance of the gold cluster shows a nonclassical behavior caused by electron tunneling between the tip and the cluster when the separation is small enough. The STM study gives 1.3×10^{-20} F for the capacitance of a cyclopentene molecule [4]. These experimental results on the capacitances of extremely small values indicate that the evaluation of the capacitances of nanostructures by a conventional classical approach is no longer valid.

Theoretically, quantum approaches to the calculation of capacitance have been formulated, and the quantum corrections caused by the electron tunneling and/or the finite density of states have been discussed [5,6]. A recent *ab initio* study shows a crossover from a classical to quantum behaviors in the capacitance of atomic junctions of several number of Al atoms as the electrode separation decreases [7]. These theories consist of several steps of computations: (i) determine the effective potential for electrons. (ii) Solve the single electron scattering problem in the potential. (iii) Calculate the nonequilibrium charge distribution by the chemical potential shift to obtain the electrochemical capacitance.

Although these methods are very accurate and adequate for the evaluation of capacitances in fully quantum regime where electron tunneling is not negligible, the computational cost will dramatically increase as the system size and/or the electrode separation increase. In particular, the evaluation of the capacitance of nanostructures which are separated by nanometers and the self-capacitances of carbon nanotubes (CNT's), for example, are very difficult by the theoretical approaches above.

Therefore, the objectives in this study are to accurately calculate the capacitances of molecules, fullerenes, CNT's and the self-capacitances by a simple *ab initio*

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approach, partitioned real-space density functional (PRDF) method [8] and to compare those with experimental ones. The PRDF method, which has been also successfully applied to the study of field evaporation from carbon nanotubes [9], is briefly described in the next section.

2 Method and model

The PRDF method based on *ab initio* higher-order finite-difference pseudopotential method [10,11] within the density functional theory (DFT) [12,13] has been recently developed for determining the electronic structures of bi-electrodes without electric current under bias voltage or in an electric field. Investigation of such systems by a standard DFT has been impossible, because electrons necessarily transfer from one electrode with higher potential toward the other electrode with lower potential under bias voltage or electric field owing to the nature of the DFT, that is, the DFT seeks the global ground state. In another words, the standard DFT determines the equilibrium ground state with one Fermi energy. The main procedure of the PRDF calculations is to divide the entire system into subsystems and to calculate the electronic wave function and electron density in each subsystem using self-consistently potential defined in the entire system. Given an excess charge Q and $-Q$ to the left and right electrodes shown in Figures 1a and 1b induced charge-density-distribution and in Figure 1c effective potential and Fermi energies, E_F^R and E_F^L are self-consistently determined. As a result, the capacitance C is easily obtained by the simple formulae

$$V = (E_F^R - E_F^L)/e, \quad C = \mathrm{d}Q/\mathrm{d}V, \qquad (1)$$

where, e is an electron charge. Since the voltage V is a function of Q, the nonlinearity is automatically included in the capacitance C. It should be noted that the electrode separation should be large enough and the bias voltage should be small enough for the condition of no electron-tunneling, because the PRDF method preserves the number of electrons in each subsystem. Therefore, the evaluation of capacitances in this study is valid only when the effect of electron tunneling is negligible.

We have chosen to study the capacitance of spherical jelliums of various electron densities to compare with those of classical counterparts. The capacitances of Si_5, fullerenes (C_{20} and C_{60}) and CNT's ((5, 0) zigzag and (3, 3) armchair nanotubes) are investigated as examples of molecules and clusters. Finally, the capacitance of a cyclopentene molecule (C_5H_8) is calculated to compare with that obtained in a recent experiment.

The technical details of numerical calculations are as follows. For exchange-correlation potential, we used the local density approximation [14,15] for spherical jelliums and the generalized gradient approximation by Perdew *et al.* [16] for the other structures. We employed the norm-conserving pseudopotentials of NCPS97 [17] based on the Troullier and Martins formalism [18]. We solved the Poisson's equation to obtain the Hartree potential in the Kohn-Sham (KS) Hamiltonian [13]. The values of Hartree potential at outer boundaries were calculated from multipole expansion up to the l = 7th Legendre functions. Both solutions of Poisson's equation and Kohn-Sham equation were obtained by the conjugate gradient (CG) method [19]. The grid spacing is 0.16 Å. We have checked that the grid spacing of 0.16 Å is fine enough for convergence of energies of a hydrogen, carbon and silicon atoms within 0.02 eV.

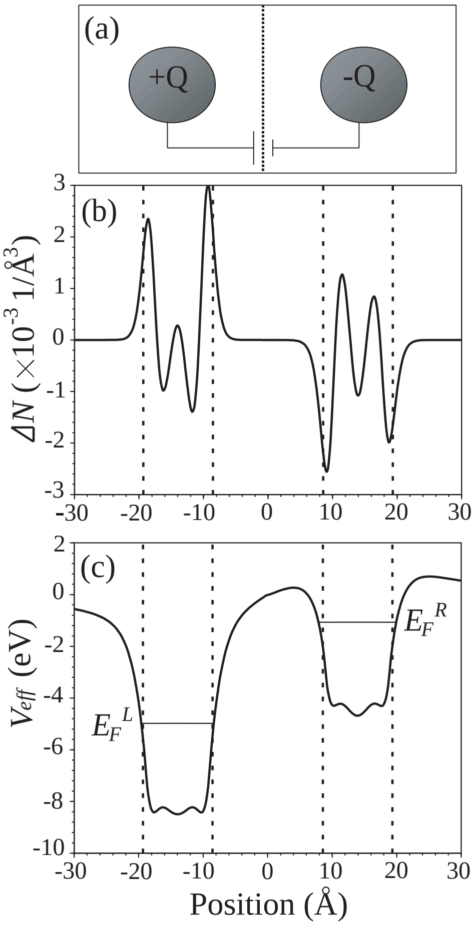


Fig. 1. Electronic states obtained by the PRDF method. (a) Schematic configuration of charged bielectrodes (spherical jelliums) under bias voltage in the partitioned space. (b) The induced charge-density-distribution ΔN and (c) the effective potential V_{eff} of spherical jelliums along the line which links the center of two spheres and two Fermi energies E_F^L and E_F^R self-consistently calculated. The bias voltage V is determined by $eV = E_F^R - E_F^L$. The electron density of the jelliums is defined by the Wigner-Seitz radius (in units of Bohr radius), $r_s = 3.86$.

3 Results and discussion

The calculated results on the capacitance of spherical jellium with radius a = 5.17 Å as a function of $1/R$ (R is the distance between the center of the two spheres) are shown in Figure 2. Closed and open circles are the results

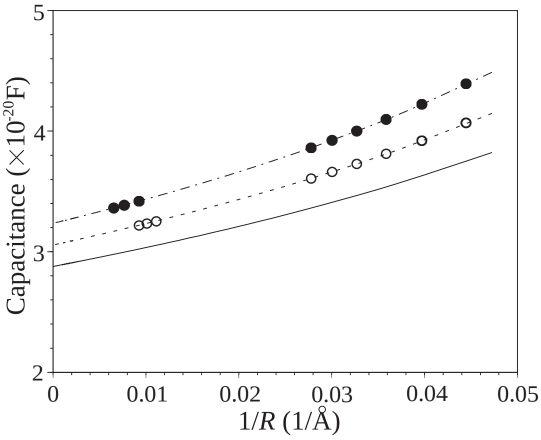


Fig. 2. Capacitances of the spherical jelliums as a function of $1/R$ (Fig. 1a). Here, R is the separation of the two sphere centers. Closed and open circles are the results obtained by the PRDF method for $r_s = 3.86,\ 2.84$, respectively. Solid line is the classical result. The dash-dotted and broken lines to fit the closed and open circles are drawn by equation (2) with the effective radius, $a = 5.82$ Å and 5.49 Å, respectively.

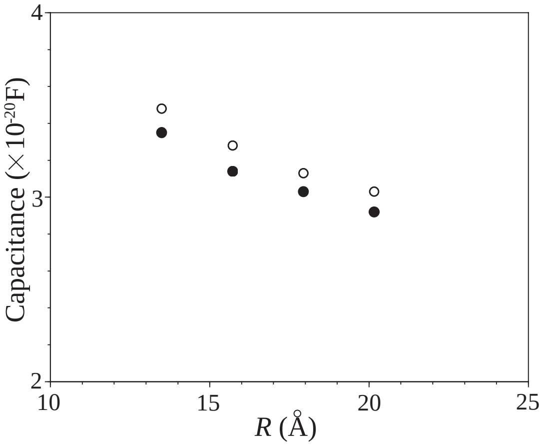


Fig. 3. Capacitances of CNT's as a function of the separation, R between the CNT axes. Closed and open circles are the results of $(5,0)$ zigzag CNT with the length of 7.2 Å and the diameter of 3.9 Å, and $(3,3)$ armchair CNT with the length of 7.3 Å and the diameter of 4.1 Å, respectively.

for electron densities of $r_s = 3.86$ and 2.84, respectively. The electron density of the jellium is defined by the Wigner-Seitz radius in units of Bohr radius, r_s. The capacitance of classical spherical bielectrode is given by the formula,

$$C = 2\pi\varepsilon_0 a(1 + m + m^2 + m^3 + 2m^4 + 3m^5 + \cdots), \quad (2)$$

where ε_0 is the permittivity of the vacuum and $m \equiv a/R$ [20]. The classical values are given by a solid line in Figure 2. In this study, we have expanded C up to the fifth-order of m in equation (2).

First, we note that the quantum capacitance of the bielectrode decreases and approaches the classical value (solid line) as the electron density increases. The reason for this property is that the effective surface position of the spheres determined by the electron density profile around the positive background charge edge shifts inward the sphere center as the electron density increases (r_s decreases), resulting in the increase in the effective separation of bielectrode. The electron-density dependent effective surface position has already been theoretically investigated by several authors [21,22] only when the surfaces are perfectly flat. Although the present surface of spheres is not flat but curved one, the tendency of the surface position on electron density is consistent with the result of Gies and Gerhardts [22].

Second, we can fit the data of closed ($r_s = 3.86$) and open circles ($r_s = 2.84$) to the dash-dotted and broken lines by choosing the radii $a = 5.82$ Å and 5.49 Å in the classical formula (2), respectively. These effective radii are larger than the radius of positive background sphere of 5.17 Å due to the leakage of electron cloud to the vacuum side. This result means that the effective radius of spherical jellium decreases as the electron density increases. This feature is consistent with a result for negligible electron-tunneling regime in a previous study [6]. It is difficult to evaluate the effective surface position (effective radius) of the spherical jellium directly from the self-consistent charge distribution because the induced charge profile is not smooth enough due to the finite size effect of the nanosized structures as clearly seen in Figure 1b for determining the accurate surface position.

Third, we obtain the value of self-capacitance of the spherical jellium from Figure 2 by multiplying the capacitance of bielectrode of $R = \infty$ by 2. It gives $6.47{\times}10^{-20}$ F, $6.11{\times}10^{-20}$ F and 5.76 $\times 10^{-20}$ F for the jelliums of $r_s = 3.86,\ 2.84$ and for the classical electrode, respectively. The classical value of self-capacitance of a spherical electrode is given by $4\pi\varepsilon_0 a$. Thus, we conclude that the self-capacitance of spherical jellium depends on the electron density through the effective radius a.

Now, we discuss the capacitance of CNT's as a typical example of nanostructures. The capacitances of an open-ended $(5,0)$ zigzag (closed circles) and a $(3,3)$ armchair (open circles) CNT's as a function of the distance, R between the two same type CNT's are given in Figure 3. We use the nanotube indices (n,m) following the abbreviations adopted in a previous study [23]. The sizes of the two CNT's are very close, *i.e.*, the diameter of the $(5,0)$ ($(3,3)$) nanotube is 3.9 Å (4.1 Å) and the length of the $(5,0)$ ($(3,3)$) nanotube is 7.2 Å (7.3 Å). As seen in the small difference in the capacitances between the two CNT's, the atomic geometry of CNT's does not influence the capacitance. The result, however, does not necessarily mean that the effect of the electronic structures of CNT's on the capacitances is negligible. Further detailed analysis is needed to clarify this in a future study.

We have calculated capacitances of CNT's with the same type as above with different length, and found that the capacitance is a linear function of the length. This linear property of capacitance enables the evaluation of self-capacitances of long CNT's. The calculated value of the self-capacitance of $(5,0)$ nanotube of 3 μm length is 1.7×10^{-17} F, which is close to the value of 3×10^{-17} F

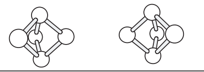
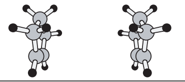
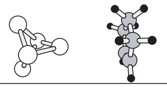
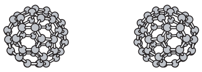
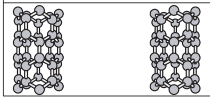
Nanostructures		R (Å)	C ($\times 10^{-20}$F)
	Si_5 - Si_5	16.0	1.9
	C_5H_8 - C_5H_8	14.3	2.3
	Si_5 - C_5H_8	15.0	2.8
	C_{20} - C_{20}	14.4	2.2
	C_{60} - C_{60}	16.0	3.5
	(5,0) tube	13.5	3.4
	(3,3) tube	13.5	3.5

Fig. 4. Capacitances of nanostructures investigated in this study. Open, shaded and closed circles are silicon, carbon and hydrogen atoms, respectively. R is the separation of the two centers of gravity of the bielectrode.

assumed in the scanning tunneling microscopy study on CB phenomena of CNT's [24].

We have also evaluated the capacitances of CNT's terminated with hydrogen. The effect of hydrogen, however, is found to be quite small. This is probably because the electron transfers from hydrogen to carbon atoms and thus the effective length of the tube remains unchanged.

Finally, we have evaluated capacitances of several type nanojunctions by the PRDF method and listed those in Figure 4. The properties obtained are summarized as follows. (i) The values of the capacitances are a few 10^{-20} F. (ii) Adsorbed hydrogen does not affect the capacitance. (iii) The capacitance of fullerene is not proportional to the number of carbon atoms in the cluster. (iv) The capacitance of CNT is almost independent of the detailed atomic geometry. (v) The capacitance of nanojunction, $Si_5{-}C_5H_8$ is compatible with the one (1.3×10^{-20} F) observed by the scanning tunneling microscopy study [4]. More precise interpretations for these properties will be given by the detailed analysis of the electronic structures of the nanojunctions elsewhere.

4 Conclusion

We have evaluated the capacitance of spherical jelliums, molecules, fullerenes and CNT's in zero electron-tunneling regime by the PRDF method. We found that the quantum capacitance of spherical jelliums decreases and approaches the classical value as the electron density increases. The capacitances of fullerenes and CNT's do not depend on the atomic geometries but on the overall shapes. The self-capacitance of nanostructures can be evaluated by the PRDF method without difficulties. The calculated capacitances of molecules and CNT's are compatible with observed ones by the scanning tunneling microscopy studies. Finally, we emphasize that the PRDF method is an ideal tool for evaluating capacitances of nanostructures under the condition of no electron-tunneling.

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