

Density Functional Theory Calculations of Quantum Capacitance and Total Surface Charge of Graphene with Varying Supercells

Kyle Alfred C. Paz¹, Stanley Lawrence B. Chua¹, Al Rey Villagrancia¹, Melanie David¹

¹ Department of Physics, De La Salle University 2401 Taft Avenue Malate 0922 Manila Philippines

*Corresponding Author: melanie.david@dlsu.edu.ph

Abstract: The properties of nanomaterials and their functionalities have long been investigated using computational methods. For this study, density functional theory, along with spline interpolation and numerical integration were utilized in modeling and finding the quantum capacitance and surface charge of graphene. This paper is focused on the relationship between the supercell size of graphene with the quantum capacitance and surface charge. The density of states (DOS) of graphene were calculated for supercell sizes 1x1, 3x3, and 5x5. The DOS of the three supercell sizes were then fitted to a quadratic spline to solve for the quantum capacitance and then numerically integrated to solve for the surface charge. Results showed that by increasing the supercell size, the values of the quantum capacitance and surface charge also increase. However, the quantum capacitance and surface charge per supercell area are approximately the same regardless of the size of the supercell. To confirm the results, parabolic and exponential fitting were applied to the quantum capacitance and surface charge curves, respectively. The coefficients of the fitted quantum capacitance per supercell area were found to be consistent regardless of the supercell size whether using a parabolic equation or exponential function. These results indicate that a small supercell would be sufficient to model larger systems in calculating quantum capacitance and surface charge in a supercapacitor device.

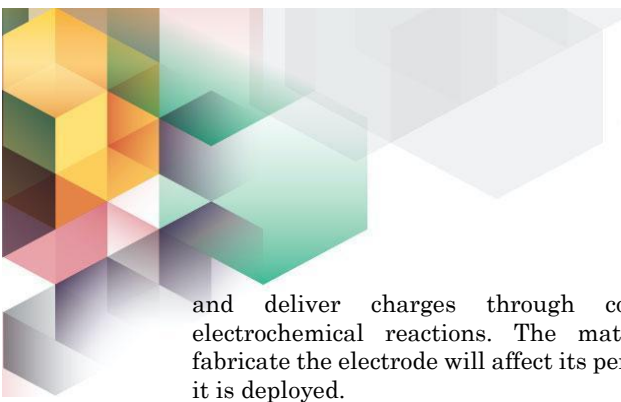
Key Words: density functional theory; density of states; graphene; quantum capacitance; surface charge; numerical discrete integration

1. INTRODUCTION

Renewable energy has gained traction in the scientific community because of its sustainability; however, its reliability fails in contrast to the use of fossil fuels. The reliance of renewable energy production on unpredictable variables such as the weather, sunlight, water supply, etc, has made it inconsistent. Developing a method to store the produced energy from renewable resources could

make up for its inconsistent production. With that being said, energy storage devices are important in the field of renewable energy.

This study focuses on the field of energy storage devices, specifically supercapacitors. The longevity of a battery and the power of a capacitor is the common description of a supercapacitor. A supercapacitor is made from two electrodes that are soaked in an electrolyte solution with a separator in between, because of this, the supercapacitor can store



and deliver charges through coulombic and electrochemical reactions. The material used to fabricate the electrode will affect its performance once it is deployed.

The properties of materials are described much better when quantified by equations. However, these equations may be too complex to solve manually. Computational methods such as numerical discrete integration and density functional theory (DFT) can be used to model these materials and to further scrutinize and explore their properties and functionalization. This study will specifically solve for the quantum capacitance and surface charge of a well-known, widely investigated and highly functionalized nanoscale material, the graphene.

Graphene is a 2-D material made out of carbon, it is arranged in hexes and has a zero-bandgap energy (Hussain, 2019). To gauge the accuracy of this study, the results were compared to an existing literature on quantum capacitance of a 1x1 graphene (Zhan, 2015). In addition, this study aims to determine the effects of supercell sizes on the quantum capacitance and surface charge values of graphene based on density functional theory, spline interpolation and numerical discrete integration. The following properties are the interest of discussion in this paper: density of states, quantum capacitance, and surface charge of graphene.

In the context of material science, the density of states is a mathematical function that gives the “number of allowed quantum states as a function of energy” that a particle can occupy in each material (Neaman, 2002). These densities of allowed states are useful in determining the concentrations of electrons and holes which will, in turn, give an approximation for the electrical conductivity of the material

The quantum capacitance and the electric double-layer capacitance (EDLC) are the contributing components of the total capacitance of a material. Their relationship is quantified through this equation.

$$C_{total} = \frac{1}{C_Q} + \frac{1}{C_{EDL}} \quad (\text{Eq. 1})$$

C_Q = Quantum capacitance

C_{EDL} = Electric double-layer capacitance

The quantum capacitance of materials comes from its electronic structure, and the EDLC comes from the interaction between the electrode and the electrolyte solutions (Zhang et.al, 2015). These two

quantities have an inverse relationship as shown in Eq. 1. The importance of quantum capacitance is greater in materials that have less occupied states near the Fermi level such as graphene and semiconductors. The formula for quantum capacitance is shown in Eq. 2. Once quantum capacitance has been calculated, the surface charge Q can then be obtained using Eq. 3 (Zhou et.al, 2021). This equation represents the cumulative charge on a specific value of voltage that is dependent on the quantum capacitance. The quantum capacitance and total surface charge were plotted against the external potential. The material that exhibits higher values of quantum capacitance is the most viable material for supercapacitor electrodes.

$$C_Q = \frac{e^2}{4kT} \int_{-\infty}^{+\infty} D(E) \text{sech}^2\left(\frac{E-\phi}{2kT}\right) dE \quad (\text{Eq. 2})$$

where:

- $D(E)$ = Density of states
- e = charge of the electron
- ϕ = Applied potential
- T = 300 K, Room temperature
- k = Boltzmann's constant

$$Q = \int_0^\phi C_Q(\phi) d\phi \quad (\text{Eq. 3})$$

where:

- C_Q = Quantum Capacitance
- ϕ = Applied potential

2. METHODOLOGY

2.1 Density Functional Theory.

The density of states of graphene was calculated using Quantum Espresso (Giannozzi et al., 2009, 2017). A k -point sampling of gamma-centered 33x33x1 was used in all systems. The cut-off energy was set to 520 eV. The exchange-correlation functional used in the calculation was the Perdew-Burke-Ernzerhof, and a van der Waals method was used as a correction. Graphene supercell sizes 1x1, 3x3, and 5x5 were chosen for this calculation as they are most used by studies such as the papers of Zhou (2021) regarding a 5x5 germanene and Zhan (2015) concerning a 1x1 graphene system. The supercell model for these dimensions is shown in Fig. 1.

2.2 Computational Method

Spline interpolation was used to construct the DOS, quantum capacitance, and surface charge functions, out of the discrete data sets. In this method, the predicted curves were divided into separate lines bounded by two data points called splines. These splines are expressed as quadratic polynomials that are evaluated at each point of the curve. The constructed quadratic functions will represent $D(E)$, $C_q(\varphi)$, and $Q(\varphi)$ found in Eq. 2, and Eq. 3. The equations were then solved using numerical discrete integration.

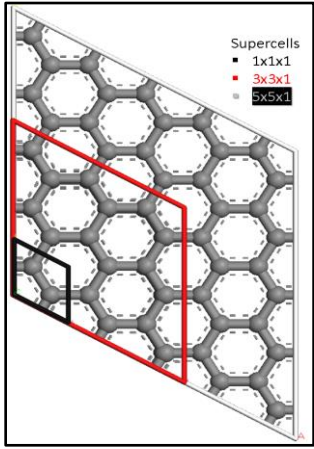


Fig. 1. Supercell model of graphene for all three spatial dimensions.

2.3 Polynomial and Exponential Fitting

A parabolic function was fitted onto the quantum capacitance curves to accurately compare the quantum capacitance values of the different spatial dimensions of graphene. The parabolic function is expressed as

$$f(x) = a(x - h)^2 + k, \quad (\text{Eq. 4})$$

where a represents the width of the parabola. The higher this coefficient is, the narrower the width of the parabola. The h and k , on the other hand, represent the vertices of the parabola.

For the surface charge curves, an exponential fit was used, and the expression of the exponential function is expressed as:

$$f(x) = ae^{bx} - ce^{-dx}. \quad (\text{Eq. 5})$$

The expression in Eq. 5 shows two terms, one with a and b coefficients, and another with c and d coefficients. The first term represents curves that are growing while the second term represents curves that

are decaying as exhibited by the signs on the exponents. The rate at which a curve grows or decays is described by the b and d coefficients, respectively. A higher b means faster growth, and a higher d , an increase in decaying rate. The other coefficients a and c represent the points in the x-axis to which the growth rate starts, and the decay rate ends, respectively. A larger a and c coefficient means that the growth or decay rate starts or ends at a point very near 0, while a lower value means they happen at a farther point.

3. RESULTS AND DISCUSSION

3.1 Fitting of the density of states to quadratic splines

The DOS functions $D(E)$ were constructed using spline interpolation for the different supercells of graphene. The original data points were then recovered to prove the function's precision and were plotted together with the fitted points as shown in Fig. 2. The x-axis represents the energy of the occupied states, and the y-axis represents the number of occupied states. We observed that as the supercell size increases, the DOS values also increase, but the peak and trough locations along the x-axis remains the same.

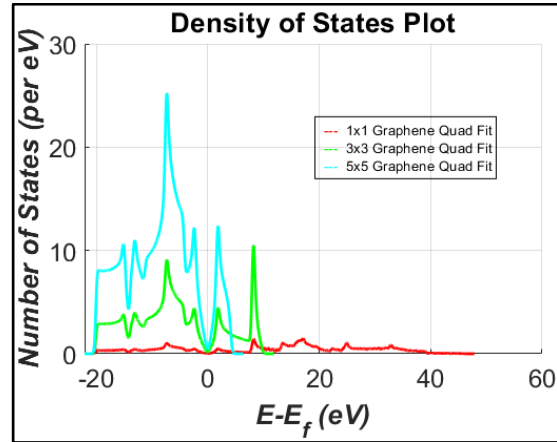


Fig. 2. The DOS for different spatial dimensions of graphene.

3.2 Solving for the quantum capacitance

With the $D(E)$ solved, we proceeded with the calculations of quantum capacitance of graphene with different supercell sizes by solving Eq. 2 using numerical discrete integration. The integral ran through the entirety of the interpolated DOS curve with potential values set to -1 V to 1 V with 30 data

points in between, the results are shown in Fig. 3. The quantum capacitance in microfarads graphed against the applied potential in volts.

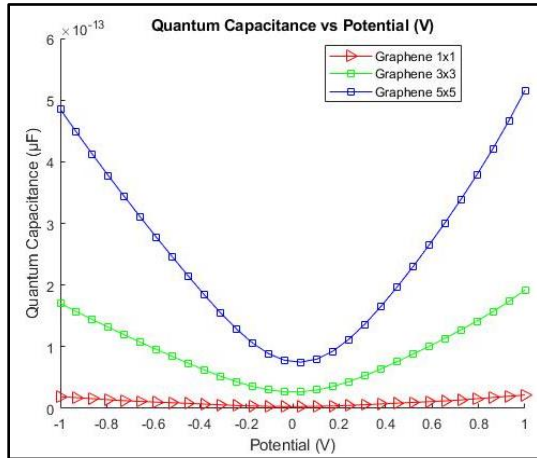


Fig. 3. Quantum capacitance of the unit cell vs the potential.

The density of states increases as the supercell dimension increases, and the same relationship is observed in the quantum capacitance values (Fig. 3). The quantum capacitance of graphene with 5x5 dimensions exhibited the highest values for quantum capacitance, while graphene with 1x1 supercell has the lowest. We further normalized the data we obtained and used cm^2 as the standard unit of area. The results are shown in Fig. 4. The x-axis is still the potential in volts, while the y-axis is the quantum capacitance in microfarads per square centimeter.

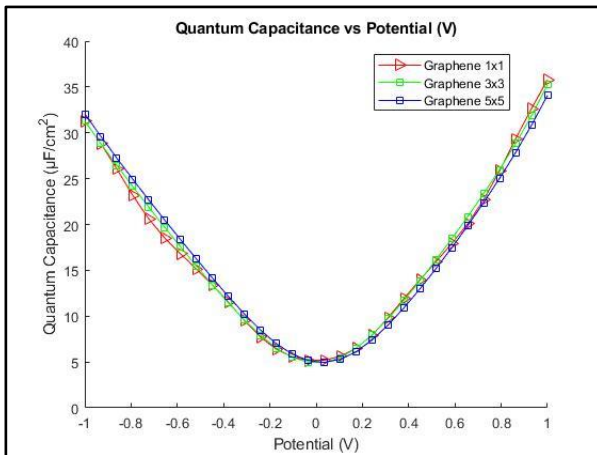


Fig. 4. Quantum capacitance per square centimeter vs the potential.

The resulting quantum capacitance values were consistent with that of the single-layer graphene quantum capacitance solved by Zhan's research in 2015. As expected, the quantum capacitance values of the different graphene supercells are now relatively closer once standardized using a unit area. There are still differences between the values, and this could be the effect of the difference between the density of states of the different graphene supercells. These discrepancies found on the different DOS curves were amplified during the calculations for quantum capacitance.

3.3 Solving for the surface charge

The resulting quantum capacitance from the previous calculation provided us with another discrete data set to be used in calculating the surface charge of graphene. A quantum capacitance function $C_Q(\phi)$ was constructed using spline interpolation. We solved Eq. 3 using numerical discrete integration once again, running the potential values from -1 V to 1 V with a 0.066 V interval. Fig. 5 shows the graph of surface charge in microcoulombs as a function of potential in volts.

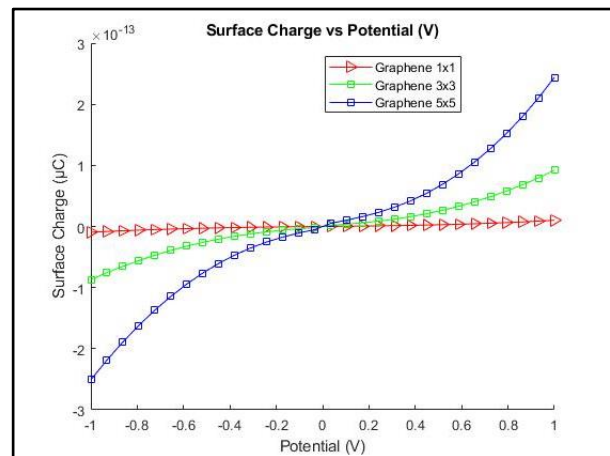


Fig. 5. Surface charge vs the potential of the different supercell sizes

As can be seen in Fig. 5, the graphene with 5x5 supercell size exhibited the most surface charge accumulation in both forward and backward bias voltage, while graphene with 1x1 supercell size demonstrated the lowest. The surface charge was then standardized using a unit area, and once again cm^2 was used.

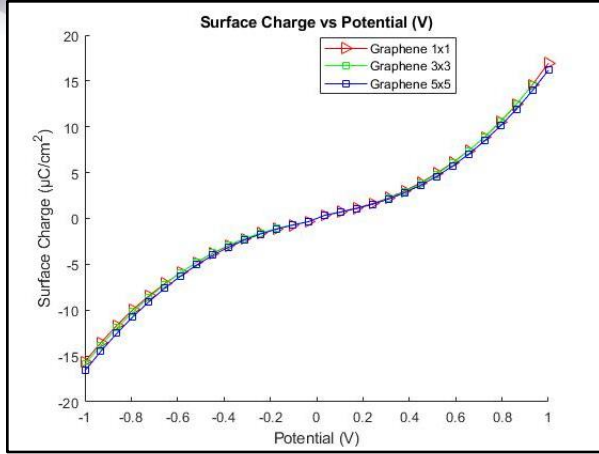


Fig. 6. Quantum capacitance per cm^2 vs the potential

Fig. 6 shows the surface charge of all graphene supercells. They all exhibited relatively similar values when standardized using a unit area. 1x1 graphene had values of -15.6214 to $+16.9351$ $\mu\text{C}/\text{cm}^2$, 3x3 graphene had values ranging from -15.9144 to $+14.5642$ $\mu\text{C}/\text{cm}^2$, and 5x5 graphene obtained values from -16.6153 to $+16.1749$ $\mu\text{C}/\text{cm}^2$. The slight differences between the supercells are again, an effect of the varying magnitudes of the DOS.

3.4 Fitting quantum capacitance to a parabolic equation.

Table. 1 Polynomial fitting of quantum capacitance.

Graphene	a Coefficients [Left]	a Coefficients [Right]
1x1	14.7330	15.6048
3x3	15.3096	15.8991
5x5	16.0845	14.9774

Table 1 summarizes the right (positive potential) and left (negative potential) coefficients of the polynomial fitting of quantum capacitance curves for different dimensions of graphene. Looking at the left of the quantum capacitance curves; the values are very near each other with a slight difference of 0.5766 between 1x1 and 3x3 and a difference of 0.7749 between 3x3 and 5x5. Nonetheless, we see that the 5x5 graphene has the highest coefficient suggesting that it has a steeper slope out of the three spatial sizes. Meaning for negative potentials, the higher the spatial size, the higher the quantum capacitance. For the positive potentials, the 3x3 and 1x1 have higher coefficients with a difference of only 0.2943 between them. This means that materials with lower spatial

sizes have higher quantum capacitance. Despite these differences, the coefficients are very close to each other. So, it can be said that increasing the spatial sizes of graphene has no significant effect on quantum capacitance.

3.5 Fitting surface charge to an exponential equation.

Table. 2. Exponential fitting of surface charge.

Graphene	Positive Side	Negative Side
1x1	$a = 1.577; b = 2.399$	$c = -1.595; d = -2.309$
3x3	$a = 1.470; b = 2.493$	$c = -1.524; d = -2.379$
5x5	$a = 1.523; b = 2.387$	$c = -1.644; d = -2.349$

Listed in Table 2 are the coefficients of the exponential fitting of surface charge curves of the different dimensions of graphene. These coefficients are divided into two groups: one decaying (negative d) and another growing (positive b). The 3x3 graphene has the highest b and d value which may mean it has the highest surface charge. For the other two dimensions, opposite trends are observed. 1x1 graphene has the faster growth rate for positive potentials while 5x5 graphene has the faster decay rate for negative potentials. However, looking at 3x3 graphene's a and c coefficients, even though it has the largest b and d coefficients, it does not necessarily mean that it has the highest surface charge values out of the three spatial dimensions. First for positive potentials, it is observed that 1x1 graphene's a value is the largest, followed by 5x5 and then 3x3. In other words, 1x1 graphene's growth rate happens at a potential nearest to 0 while for 3x3 graphene its growth rate happens at a potential farthest from 0. This result shows that while 3x3 graphene's growth rate is larger than 1x1 graphene, it does not happen until a larger potential value is applied. Hence, for positive potentials, 1x1 graphene still obtains the higher surface charge value for low values of potential. Looking at the negative potential, 3x3 graphene still has the lowest c coefficient. So, while it has the highest d value, this does not happen until a high negative potential value is applied. Moreover, 5x5 graphene has a higher d value than 1x1 graphene and the highest c value meaning it has the highest surface charge values for low potentials. And so, the trend persists, similar to section 3.4, increasing the spatial size increases the surface charge values only for negative potentials, the opposite trend is observed for positive potentials.



4. CONCLUSIONS

The quantum capacitance and surface charge were dependent on the DOS functions. The DOS of graphene as the supercell dimension increases only increases in magnitude, but its behavior such as peak locations remains relatively unchanged. Without doing any of the calculations, one can make an intelligent guess that the bigger supercell-sized graphene will exhibit the biggest quantum capacitance and surface charge values. This trend is true as shown in Figs. 3 and 5. The influence of the supercell size waned when we standardized the values according to a unit area (cm^2). However, there are still slight differences in values of the three supercell sizes.

In analyzing the parabolic equation fitting of the quantum capacitance curves, the assumption that higher dimensions of graphene can attain higher values of capacitance was confirmed for only negative potentials. For the surface charge curves, it is only in the negative part of the curve that a higher dimension of graphene can gain higher values of surface charge. For the positive part, it can be seen from Table 2 that the 1x1 graphene had the highest growth rate among the three dimensions of graphene. Nevertheless, the differences between the coefficient values are so small that it can be said that changing spatial dimensions have no effect on the material's quantum capacitance.

This study was able to find the relationship between supercell sizes and quantum capacitance, but there are more quantities that could affect it. We recommend further investigation of the effects of doping, introducing vacancies, and interplanar distance among others to establish graphene comprehensively and practically as a viable material for supercapacitors. Assuming that the results of this study are consistent with other materials, then it is better to use smaller supercell sizes in modeling to save computational cost. And this study was able to show that supercell sizes have little effect on the quantum capacitance and surface charge of graphene.

5. ACKNOWLEDGMENTS

We would like to thank the Computational Materials Design Research Group in De La Salle University for supporting this study towards completion.

6. REFERENCES

Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., ... Wentzcovitch, R. M.

(2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39), 395502. doi:10.1088/0953-8984/21/39/395502

Giannozzi, P., Andreussi, O., Brumme, T., Bunau, O., Buongiorno Nardelli, M., Calandra, M., ... Baroni, S. (2017). Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of Physics: Condensed Matter*, 29(46), 465901. doi:10.1088/1361-648x/aa8f79

Hussain, F., Imran, M., Rasheed, U., Khalil, R. M. A., Rana, A. M., Kousar, F., ... Hayat, S. S. (2019). A First Principle Study of Graphene/Metal-Oxides as Nano-Composite Electrode Materials for Supercapacitors. *Journal of Electronic Materials*. doi:10.1007/s11664-019-07064-2

Kan, E., Li, Z., & Yang, J. (2011). Graphene Nanoribbons: Geometric, Electronic, and Magnetic Properties. *Physics and Applications of Graphene - Theory*. doi:10.5772/14112

Neamen, D. (2002). *Semiconductor Physics And Devices* (3rd ed.). McGraw-Hill Science/Engineering/Math.

Wang, L., Wu, Y., Jia, W., Gao, W., Chi, X., Lawrence, L.-W. W., & Wang, L.-W. (2011, November 1). Large scale plane wave pseudopotential density functional theory calculations on GPU clusters. <https://dl.acm.org/doi/10.1145/2063384.2063479>.

Xia, J., Chen, F., Li, J., & Tao, N. (2009). Measurement of the quantum capacitance of graphene. *Nature Nanotechnology*, 4(8), 505–509. doi:10.1038/nnano.2009.177

Zhan, C., Neal, J., Wu, J., & Jiang, D.-en. (2015). Quantum Effects on the Capacitance of Graphene-Based Electrodes. *The Journal of Physical Chemistry C*, 119(39), 22297–22303. doi:10.1021/acs.jpcc.5b05930

Zhou, Q., Ju, W., Yong, Y., Liu, Y., & Li, J. (2021). Quantum capacitance of supercapacitor electrodes based on germanene influenced by vacancy and co-doping: A first-principles study. *Computational Materials Science*, 188, 110131. doi:10.1016/j.commatsci.2020.110131