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Molecular Electrostatic Potential Devices on Graphite and Silicon Surfaces

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We demonstrate that molecular gates using molecular electrostatic potentials (MEP) can be used on hydrogen-passivated silicon substrates without any disturbance of their behavior in vacuum; however, the use of graphite as a substrate strongly affects such behavior. As expected, the substrate may become one more design variable. The ability to have several substrate alternatives is very important for the practical implementation of this new scenario based on molecular potentials. In general, the effect of the substrate can be predetermined by calculating the MEP of the surface as this indicates how strongly its intrinsic potential is.

1. Introduction

It has been demonstrated using reliable ab initio techniques that information can be coded using molecular electrostatic potentials (MEP).[1−9] This represents a new alternative to the conventional charge−current approach used in standard electronics. Few molecules were found to function as molecular OR[10] and AND logical gates.[11] Present computers perform calculations reducing the information to binary notation whereby the only two binary digits (bits) are 1 and 0, which also can be assigned to pairs of logical variables or states such as TRUE or FALSE, ON or OFF, HIGH or LOW, POSITIVE or NEGATIVE, respectively. In binary notation, the number nine can be written as 1001, requiring at least four binary digits (bits). Operations between binary variables are performed using logical gates such as the NOT, AND, OR. For instance, the simplest gate is the NOT, which yields 0 if the input is 1 and yields 1 if the input is 0. The AND gate has two or more inputs, and its output is 1 if all inputs are 1 and 0 if any input is 0. The OR-gate yields a 0 when all inputs are zero and 1 when any input is 1. Interestingly, these gates can be combined to make adders, multipliers, integrators, etc. In principle, we can solve numerically, using binary logic gates, any operation that we can imagine. Earlier calculations of molecular devices using electrostatic potentials were performed with the molecular gate in vacuum and excited by the electrostatic potential of small molecules. In this work, we show how the substrate affects the MEP device. We test substrates on a molecule, which has been demonstrated to be an OR-gate in vacuum.[11] The effect of the substrate on the molecular devices is of paramount importance in the theoretical proof-of-concept for this new scenario for molecular computing. In general, any approach that uses molecules or nanosized devices should consider the effect of the environment in their behavior as forces from the environment may be of the same order of magnitude as those used to represent the information in small molecules.

We test the effect on a molecular OR-gate of two substrates, planes of graphite and a hydrogen-passivated surface of silicon. The electrostatic potential of water molecules is used to model the inputs to the logical gate.

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2. Computational Methods

2.1. Ab Initio Calculation of MEP Digital Devices. The electron density ρ in a molecule or molecular systems is defined as

$$\rho(\vec{r}_1) = N \int \psi^*(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N)\psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N)\mathrm{d}\tau_2\cdots\mathrm{d}\tau_N \quad (1)$$

where $\psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N)$ and $\psi^*(r_1,\vec{r}_2,\cdots\vec{r}_N)$ are the wave function and its complex conjugate and N is the total number of electrons. The MEP, $V(\vec{r})$, is calculated from the nuclei and electron density contributions,[12]

$$V(\vec{r}) = \sum_i \frac{Z_i}{|\vec{R}_i - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}\mathrm{d}\tau' \quad (2)$$

where Z_i is atomic number of atom i located at $\vec{R}_i$. The MEP can be calculated using pure wave function methods[12−14] or using density functional theory.[15−17] The actual molecular gate was optimized with the water molecules as inputs (Figure 1) using the B3PW91[18−20] functional and the 6-31G(d) basis set as shown in ref 7. For studying the effect of the substrate, layers of graphite and hydrogen-passivated silicon are optimized first, and then the molecule is set at 4.00 Å for the graphite and for the silicon substrates. Finally, the MEP is calculated using HF/STO-5G and the B3PW91/LANL2DZ to study the effect of the graphite and the silicon hydrogen-passivated substrate, respectively. These two levels of theory have been successfully used in the past.[2,3,7,11,21,22] All these calculations are performed using the GAUSSIAN 03 program.[23]

2.2. MEP of the Components of a Computational Logic System. Figure 2 shows the MEP of the molecular device and the water molecule used as the input to the device. The color-coded scale ranges from −0.2 to 0.2 V covering colors from red to blue, respectively. Any potential smaller than −0.2 V is represented by red. Potentials larger than 0.2 V are represented by blue. This color scale allows us to precisely determine if a region in the molecule shows negative or positive potentials. As expected, potentials in the neighborhood of the nuclei are positive showing a blue region when the atoms are exactly on the MEP plane. The selection of the electrostatic

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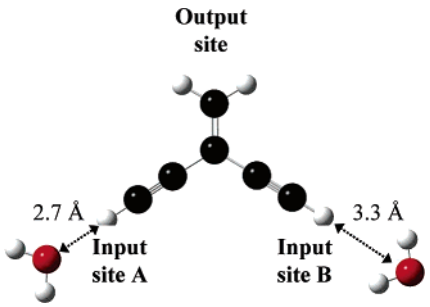


Figure 1. The OR-gate based on 1,1-diethynylethene (DEE) also known as 1,4-pentadiyne, 3-methylene. The two water molecules in the figure provide the negative and positive potentials to the gate inputs, A and B. The output is read from the "Output site".

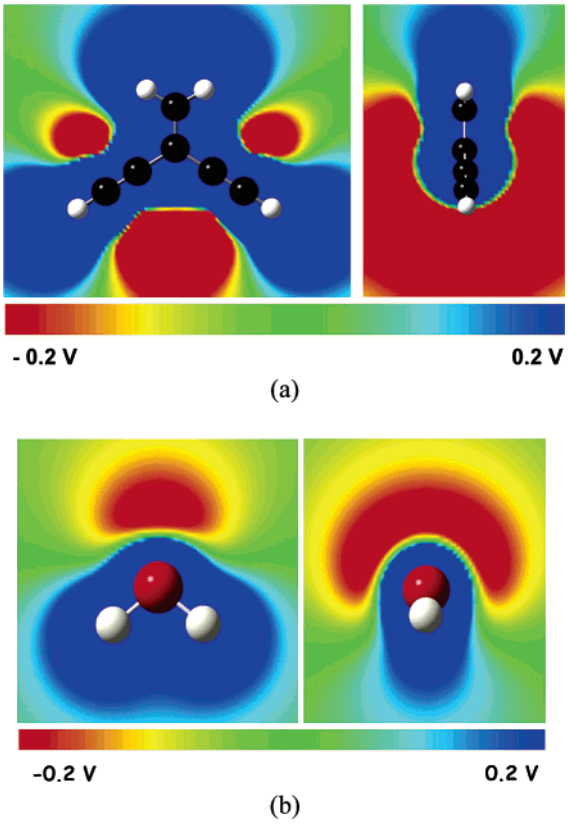


Figure 2. MEP of DEE (a) and water (b) molecules.

potentials of water to simulate an input in the molecular gates is simply based on its dipole moment. There is no special constraint other than the need to have a simple dipolar molecule, which unambiguously shows its polarity. In principle, any pair of positive and negative molecular potentials could be used for proving the concept.

Figure 2a shows on the left the MEP of the 1,1 diethynylethene (DEE) molecule on a plane containing the molecule (horizontal plane). The perpendicular view on the right side of Figure 2a shows the MEP on a plane perpendicular to the molecular plane that includes the C_{2v} axis of the molecule. Thus, only two carbon atoms lay on this perpendicular plane; all other atoms are above or below the plane. Therefore, the two lower hydrogen atoms show a full blue color on the left view of Figure 2a. However, on the right view, they show a mix of red and blue colors, because these hydrogen atoms are not on the plane of the MEP. The MEPs clearly indicate the effects of charge accumulation in a molecule. For instance, the red regions are due to the presence of double and triplet bonds in the DEE molecule or to the two lone pairs in the water molecule.

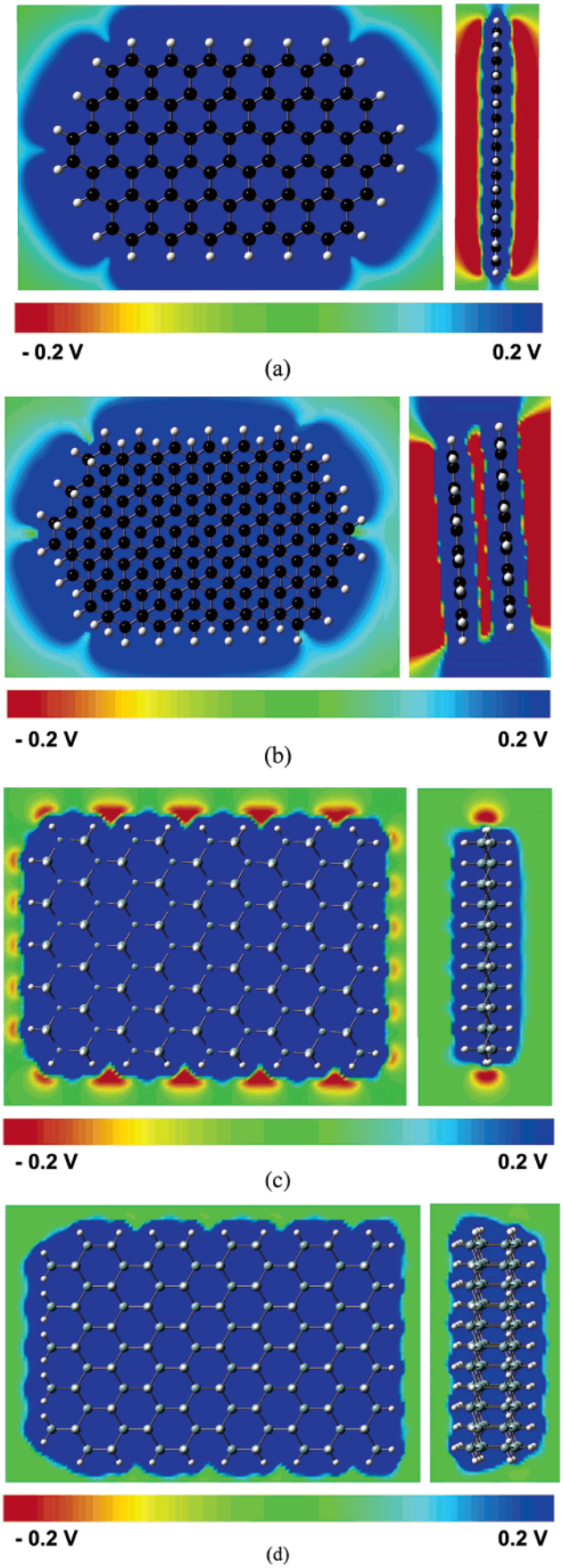


Figure 3. The MEP of the graphene used as the substrate: (a) one layer and (b) two layers. The MEP for H-passivated silicon used as a substrate: (c) one layer and (d) two layers. As a reference for the size, the C−H bonds are 1.07 Å, the C−C bonds are 1.42 Å, the Si−H bonds are 1.47 Å, and the Si−Si bonds are 2.34 Å.

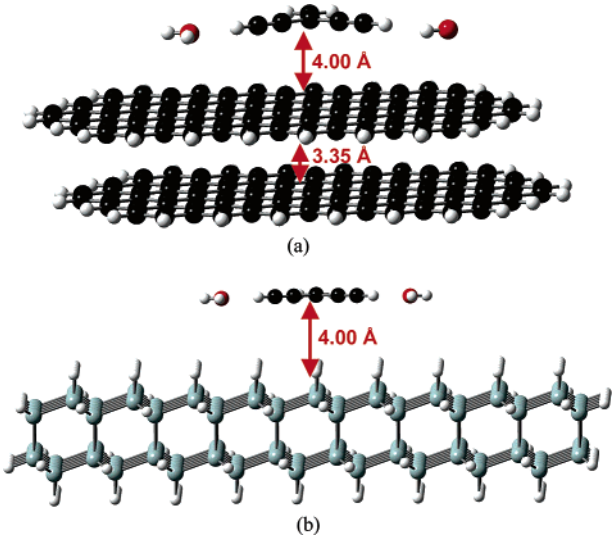


Figure 4. The molecular logic device on a substrate of (a) graphite and (b) H-passivated silicon. The molecule is 4.00 Å above of the substrates. For each case, calculations are performed with one and two layers.

Unambiguously, for the simple case of water, the oxygen side can be used as a negative potential probe and the hydrogen side can be used as positive.

Figure 3 shows the MEP of graphene and silicon sheets. The most striking difference between the two surfaces is the potential distribution on the active sites. For graphene, we calculate the MEP on a surface of one sheet and two sheets. The results are very similar. Both show a strong positive potential on the plane of the sheets and a strong negative potential above and below the surfaces. We can notice the negative potential between sheets in Figure 3b; this channel becomes a conduction path for positive ions such as Li^+ in lithium-ion batteries. Notice that the top view in Figure 3b shows all atoms from the two sheets. In this case, the separation between sheets is chosen to be 3.35 Å, which corresponds to the experimental value in graphite.[24] These strong changes in the MEP at neighborhoods of graphite require that the substrate be fully considered in the design of the gates to unambiguously determine the behavior of molecules passing information encoded in molecular potentials.

On the other hand, the silicon sheets show a more relaxed potential distribution at the neighborhood of the surfaces. Figure 3, panels c and d, corresponding to one and two silicon sheets, respectively, yield a potential practically near to zero for both cases. This is confirmed by the green regions, which show up near the sheets in the case of Figure 3, panels c and d, as opposed to the red regions in Figure 3, panels a and b.

3. Results and Discussion

Figure 4 shows the supported molecular gates in graphite and silicon sheets.

Figures 5−7 show several of the results of this work; a complete summary is given in Table 1. The so-called truth tables define the operation of each gate. Since the OR-gate has two inputs, A and B, there are four possible input combinations: 00, 01, 10, and 11. Thus, for an OR-gate, the outputs are 0, 1, 1, and 1, respectively. For an AND gate, the outputs are 0, 0, 0, and 1, respectively. By symmetry considerations, the 01 is identical to the 10, and thus we just need to analyze three combinations of inputs for the gate in each substrate.

Figure 5 shows the case when the two inputs are negative (00) for the molecular gate with and without the substrates.

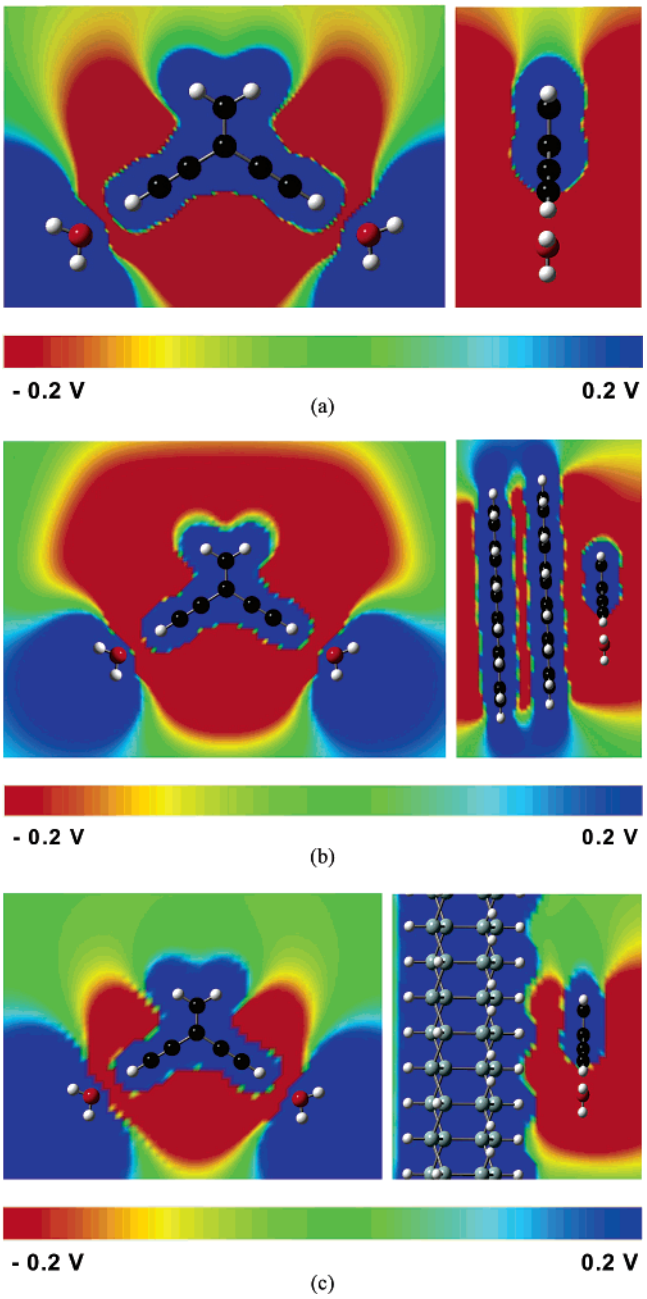
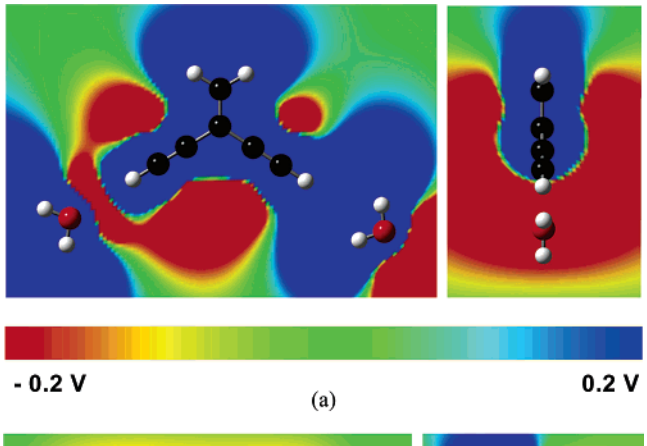
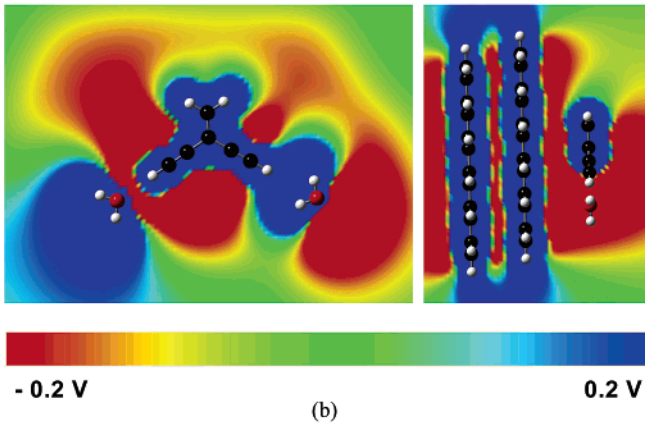


Figure 5. The MEPs for (a) the isolated molecular gate in a vacuum and over substrates of (b) graphite and (c) H-passivated silicon when the two inputs to the gate are negative.

Figure 5a shows the isolated molecule in vacuum. The application of the 00 inputs using the negative side of the water molecule in the inputs of the gate yields a slightly negative potential at the output site. The green-yellow region is unambiguously negative in the range of ∼0.1 V. The introduction of the two negative potentials of water changes the MEP of the isolated molecule (Figure 2a), which had only three small regions of negative potential, covering most of the molecule with negative regions. The strong negative potential when one small graphene sheet is used washes out the potential at the output (not shown) because of the border effects; however, potentials are back to normal if one or two sheets of graphene are used, as shown in Figure 5b. This is perhaps a more realistic situation as a few layers of graphene would be present in practice. Surfaces not shown in this paper can be seen in Supporting Information.





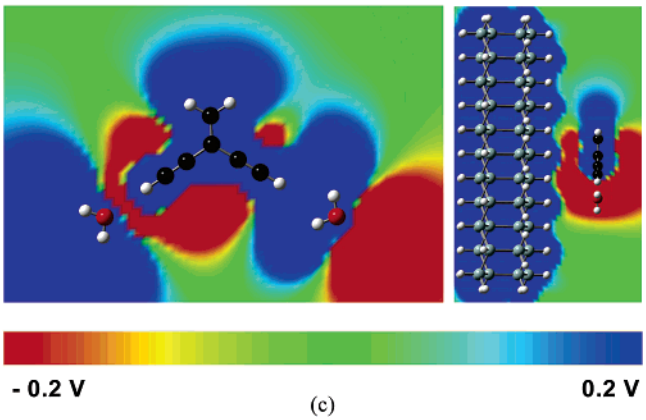
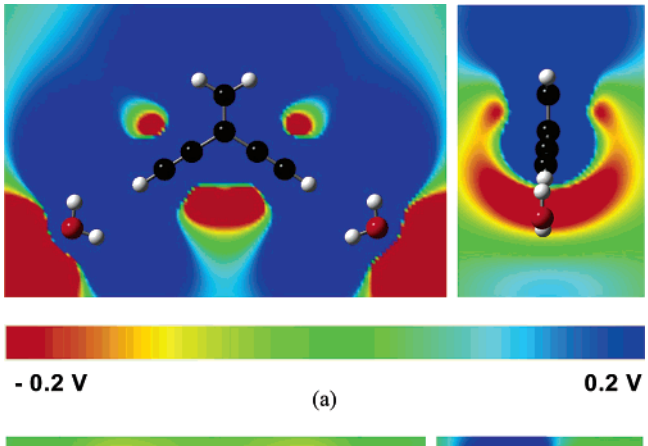
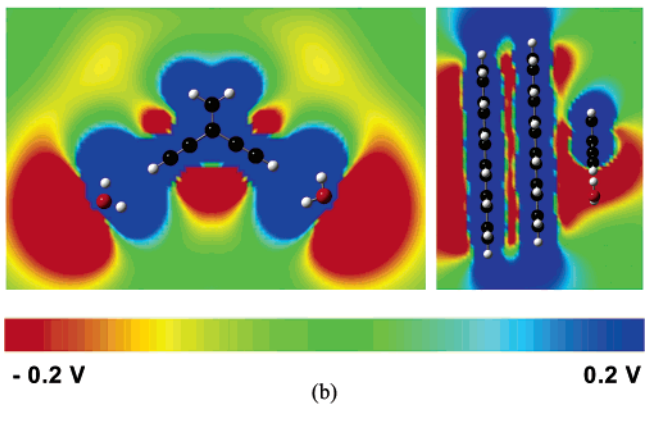


Figure 6. The MEPs for (a) the isolated molecular gate in vacuum and over substrates of (b) graphite and (c) H-passivated silicon when one input is negative and the other is positive.

On the other hand, the passivated silicon substrates do not change much of the MEP distribution obtained with a single molecule. Figure 5c shows the MEP when a double layer of passivated silicon atoms is used. The results are identical as when one layer of passivated silicon atoms is used (not shown). This is because of the low potentials shown by the isolated silicon layers in Figure 3, panels c and d; thus, the effect on the molecular gate is minimum.

Figure 6 shows the MEPs when one input is positive and the other is negative (01). The isolated molecule yields a well-defined positive potential at the output. However, when two sheets of graphene are used, the molecule yields a negative potential due to the strong negative potential of the graphene layers able to shift the positive values to the negative side. The silicon substrate does not affect strongly the molecular potentials at the output site; practically, the potential distribution is very similar to the one produce by the isolated molecule.





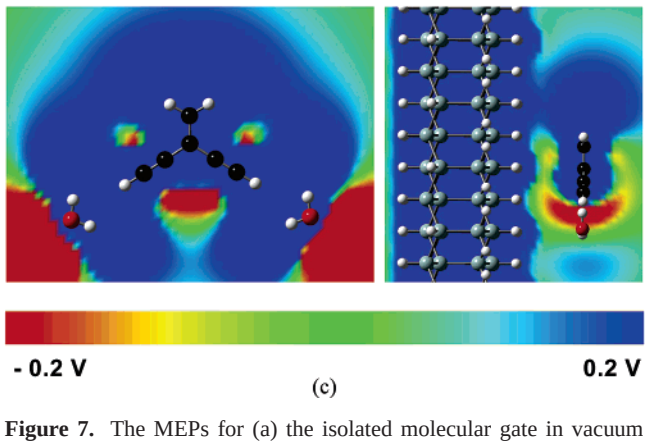


Figure 7. The MEPs for (a) the isolated molecular gate in vacuum and over substrates of (b) graphite and (c) H-passivated silicon when the two inputs to the gate are positive.

TABLE 1: Truth Tables for the MEP Gate with and without Substrates

potentials		logical			one sheet	two sheets	one sheet	two sheets
A	B	A	B	isolated	graphene	graphene	silicon	silicon
−	−	0	0	0	0	0	0	0
−	+	0	1	1	0	0	1	1
+	−	1	0	1	0	0	1	1
+	+	1	1	1	1	1	1	1
				OR	AND	AND	OR	OR

Finally, Figure 7 shows the case when the two inputs are positive (11). The isolated molecule and the molecule with the two substrates yield a positive potential at the output site. Graphite is the most difficult, as the graphene layer tends to shift potentials to negative values.

Results of all these calculations are summarized in Table 1. We can conclude from Table 1 that the use of graphite as substrate requires the redesign of the molecular device because

of the strong effect of the negative potential on its surface. The OR-gate in vacuum becomes an AND gate on graphite. However, hydrogen-passivated silicon surfaces do not change the behavior that is shown in vacuum.

4. Conclusions

We demonstrate that molecular gates using MEPs can be used on hydrogen-passivated silicon substrates without any disturbance of the behavior that the molecular gate had in vacuum; however, the use of graphite as a substrate strongly affects such behavior. As expected, the substrate becomes one more design variable if it strongly affects the potentials on its surface. The ability to have several substrate alternatives is very important for the practical implementation of the molecular potentials scenario. In general, the effect of the substrate can be determined by calculating the MEP of a surface as this indicates how strongly its intrinsic potential may affect the molecular device.

Acknowledgment. We thank the very constructive comments of the reviewers, and we would like to quote a passage of one of their reviews regarding this MEP scenario: "...the so-called *Seminario Computing*, which is the use of virtual photons or electrostatics ...". We acknowledge financial support from the U.S. Army Research Office and the U.S. Defense Threat Reduction Agency (DTRA).

Supporting Information Available: Complete figures and table including all cases not shown in Figures 3, 5, 6, and 7 as well as Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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