PHYSICAL REVIEW B **77**, 045433 (2008)

Calculating interaction between a highly charged high-speed ion and a solid surface

Yoshiyuki Miyamoto[1] and Hong Zhang[2]
[1]*Nano Electronics Research Laboratories, NEC Corp., 34 Miyukigaoka, Tsukuba 305-8501, Japan*
[2]*School of Physical Science and Technology, Sichuan University, Chengdu 610065, China*

(Received 3 September 2007; revised manuscript received 7 November 2007; published 30 January 2008)

A density functional technique for calculating interactions between highly charged ions and solids is presented, and the application of this technique to the simulation of an Ar^{7+} ion passing through a graphene sheet is demonstrated. The simulation is initiated with electronic states obtained by superimposing the individual electronic states of an ion and a solid. When the ion starts to move, the real-time propagation of all electron wave functions is treated. Also presented is a technique for gradually accelerating an ion up to a targeted velocity in order to minimize electronic excitations in the ion even without interaction with a solid surface. These techniques are suitable for analyzing bombardment of solids by highly charged, high-speed ions.

DOI: 10.1103/PhysRevB.77.045433 PACS number(s): 79.20.Rf, 73.22.−f, 02.70.−c, 71.15.Mb

Clarifying the interactions between highly charged ions and solid surfaces is important for understanding the structural changes induced in solid surfaces by bombardment with a focused ion beam[1] or with highly charged ions.[2] Precise understanding of the structural changes requires the use of computational analysis. A promising approach to obtaining such an understanding is first-principles calculation based on the density functional theory[3] (DFT) because it is free from adjustable parameters. However, it has not been directly applied to the simulation of ion bombardment and subsequent surface reconstruction because of a technical problem: the self-consistent iterations used in DFT for solving the Kohn-Sham equation[4] result in charge transfer from a solid to an ion even when they are distantly separated.

Charged objects distantly separated can be treated within the space-partitioned DFT.[5] This fixes the number of electrons within a given partition in real space and, thus, separates the charged objects from each other. However, the method used for determining the partitions becomes ambiguous when the charged objects become closer and closer, as when ions collide with a solid surface. In such a case, the electron-transfer dynamics throughout the collision must be treated instead of fixing the number of electrons in partitioned areas.

We have developed an approach to expressing the interaction of a highly charged ion with a solid surface. First, we separately calculate the electronic structures of the ion and the surface within DFT by using the same unitcells under periodic boundary conditions. Second, we determine the initial condition of the electronic systems by superimposing the results calculated for the separate systems. While this is not a standard practice with DFT, it is practical. Finally, we start the real-time propagation of electron wave functions on the basis of time-dependent DFT (TDDFT),[6] while molecular dynamics (MD) simulation is performed within the Ehrenfest scheme,[7] with the initial velocities for ions set to express the ion incidence. This combination of real-time TDDFT and MD simulation is described elsewhere.[8]

Pioneering works[9,10] took an approach to treating the real-time propagation of electron wave functions that is similar to the present one. They also recognized that it is crucial to express the charge-transfer dynamics upon impact of a charged ion with a solid surface. They used a simple jellium slab model; the target material is modeled as a simple metal, and the projectile ion is modeled as a Gaussian-type potential with a fixed trajectory. The present approach uses a more realistic model; the individual atoms in the target material are taken into account as well as the dynamics of all valence electrons.

In this paper, we demonstrate a numerically stable simulation of an Ar^{7+} ion that is initially separated from a graphene sheet and then passes through the center of a hexagon of the graphene sheet with an incidence kinetic energy of 5 keV. This simulation expresses the subsequent charge redistribution while maintaining numerical stability. We also demonstrate the induction of intra-ion excitation even without interaction with the target induced by suddenly imparting to an Ar^{7+} ion an extremely high velocity with a corresponding kinetic energy of 500 keV. This excitation can be minimized by gradually accelerating the ion to high velocity.

First, we generalize our scheme for calculating interactions between charged objects that are initially separated and then come closer together. We emphasize that the projectile ion has a valence electron that is different from that used in previous simulations, which used H^+ ions[11] and Ar^{8+} ions.[12] For system A, we obtain charge density $\rho_A(\mathbf{r})$ and a set of Kohn-Sham wave functions $\{\psi_1^A, \psi_2^A, \ldots, \psi_{N_A}^A\}$ as eigenstates of the Kohn-Sham (KS) Hamiltonian $H_A^{KS}[\rho_A(\mathbf{r})]$. For system B, we obtain $\rho_B(\mathbf{r})$ and $\{\psi_1^B, \psi_2^B, \ldots, \psi_{N_B}^B\}$ with the Kohn-Sham Hamiltonian $H_B^{KS}[\rho_B(\mathbf{r})]$. Rigorously speaking, electrons in these systems should belong to different Kohn-Sham Hamiltonians, so corresponding Kohn-Sham wave functions must belong to different Hilbert spaces.

Suppose systems A and B coexist in the same unitcell. The Kohn-Sham Hamiltonian of $\rho_{A+B}(\mathbf{r}) \equiv \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$ does not correspond to $H_A^{KS}[\rho_A(\mathbf{r})] + H_B^{KS}[\rho_B(\mathbf{r})]$ because the exchange-correlation potential of the Hamiltonian is a nonlinear functional with respect to the charge density. However, when the vacuum region of the unitcell is large enough for the tail of the total potential (Hartree-exchange-correlation potential plus potentials of all ions) to vanish from system A around system B and vice versa, and to make nonoverlapping wave functions, $H_A^{KS}[\rho_A(\mathbf{r})] + H_B^{KS}[\rho_B(\mathbf{r})]$ is very close to $H_{A+B}^{KS}[\rho_{A+B}(\mathbf{r})]$. Therefore, if systems A and B are distantly located from each other in a large unitcell, a self-consistent

©2008 The American Physical Society

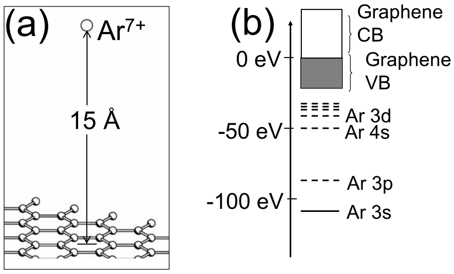

FIG. 1. (a) Atomistic configuration of Ar^{7+} ion targeted at graphene sheet below. A fragment of a periodic cell of a 5×5 unitcell of the sheet is displayed. (b) Schematic of electronic structure as a superimposition of a single graphene and the Ar^{7+} ion in the same unitcell of (a). Solid and dotted bars respectively represent half-occupied and empty levels of Ar^{7+} ion; solid and white boxes respectively represent valence bands (VBs) and conduction bands (CBs) of graphene sheet.

field (SCF) can be obtained without having to constrain the number of electrons[5] if the occupation numbers of electrons for the set of Kohn-Sham wave functions $\{\psi_1^A, \psi_2^A, \ldots, \psi_{N_A}^A, \psi_1^B, \psi_2^B, \ldots, \psi_{N_B}^B\}$ are assigned in accordance with the electron occupations of the original separated systems.

The initial conditions for the electronic system when performing the TDDFT-MD simulation are

$$\rho_{AB}(\mathbf{r},t=0) \equiv \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) \tag{1}$$

and

$$\{\psi_1^{AB}(\mathbf{r},t=0), \psi_2^{AB}(\mathbf{r},t=0), \ldots, \psi_{N_{AB}}^{AB}(\mathbf{r},t=0)\} \equiv \{\psi_1^A(\mathbf{r}), \ldots, \psi_{N_A}^A(\mathbf{r}), \psi_1^B(\mathbf{r}), \ldots, \psi_{N_B}^B(\mathbf{r})\}. \tag{2}$$

We initiate real-time propagation of the Kohn-Sham wave functions based on the TDDFT by solving

$$i\hbar \frac{\partial \psi_n^{AB}(\mathbf{r},t)}{\partial t} = H_{AB}^{KS}[\rho_{AB}(\mathbf{r},t)]\psi_n^{AB}(\mathbf{r},t). \tag{3}$$

Simultaneously, we perform MD simulation for all ions in accordance with Newton's equation of ions:

$$\mathbf{F}_I = M_I \frac{d^2\mathbf{R}_I}{dt^2}, \tag{4}$$

where $\mathbf{F}_I$ denotes the force on ion I, $\mathbf{R}_I$ denotes the coordinates of the force, and M_I is the mass of ion I. Force $\mathbf{F}_I$ is determined by the Hellmann-Feynman force, so the MD simulation is within the Ehrenfest approximation.[7] Now let us consider an example. Figure 1(a) schematically illustrates an Ar^{7+} ion directly above the center of a hexagon of a graphene sheet at a height of 15 Å. In this supercell, the vacuum region normal to the sheet is taken as 30 Å, and the lateral periodic boundaries correspond to the 5×5 periods of the primitive unitcell. The superimposition of individual electronic structures in this unitcell is schematically illustrated in Fig. 1(b). Many empty levels of the Ar^{7+} ion are located below the graphene valence bands, so the assignment of occupation numbers should be made in accordance with the original occupations of the separate systems. This superimposed electronic structure is used as the initial condition for the TDDFT-MD calculation, in which an initial velocity is imparted in the direction normal to the graphene sheet to an Ar^{7+} ion; the velocity has a corresponding kinetic energy of 5 keV. Using a periodic supercell requires that we consider the forces acting on repeated graphene sheets and Ar^{7+} ions. However, even if the Coulomb potential of Ar^{7+} ions was unscreened, the error in the Coulomb forces originating from two Ar^{7+} ions in neighboring cells would be marginal since the current supercell has a large vacuum distance[13] (30 Å) and the Ar ion has a high kinetic energy (5 kev), so the trajectory of the ion is less sensitive to Coulomb forces. These forces cause an accuracy problem only when the ion has low velocity.

Next, we demonstrate the numerical stability of this TDDFT-MD simulation, in which an Ar^{7+} ion passes through the center of a hexagon of a graphene sheet. The calculations for the static electronic structures of the individual systems and the TDDFT-MD simulation of the superimposed systems were performed using the local density approximation of DFT with the functional form[14] obtained by electron-gas calculation.[15] A plane wave basis set with a cutoff energy of 40 Ry was used to express the valence wave functions, and the interactions between the valence electrons and ions were expressed using the separable form[16] of norm-conserving soft pseudopotentials.[17] The Γ point was used for momentum space integration. For the real-time TDDFT simulation, the interval of time step Δt was set to 1.21×10^{-3} fs (fs$=1.0 \times 10^{-15}$ s). The SCF relation between the time-propagating Kohn-Sham wave functions and the Hartree-exchange-correlation potential was maintained throughout the simulation.[8] The electron occupation numbers were fixed at the levels shown in Fig. 1(b).

Classical MD was performed using the computed Hellmann-Feynman forces, which were derived from the gradients of the DFT total energy[18] with respect to the ion coordinates. This approximation is validated by the total-energy conservation rule, as shown later.

Figure 2(a) shows the time evolution of the atomic position of an Ar^{7+} ion above a graphene sheet after a velocity was suddenly imparted to it with a kinetic energy of 5 keV. Figure 2(b) shows that there was good conservation of the potential energy (DFT total energy[18]) plus kinetic energies of all ions in the unitcell, demonstrating that the SCF is sufficiently stable under the present initial condition of the electronic structure. That is, simply superimposing the individual electronic states of an isolated Ar^{7+} ion and an isolated graphene sheet is sufficient.

Figure 2(c) shows the time evolutions of the occupied states (solid curves) and empty states (dotted curves). It illustrates the effect of the Coulomb potential of an Ar^{7+} ion on graphene valence electrons. Up to the moment the ion passed through the graphene sheet, the levels of the graphene valence and conduction bands were lower although some of the conduction bands were only weakly affected. The levels subsequently increased as the Ar ion was leaving, but they never returned to their original values.

Suppose the incident Ar^{7+} ion is completely neutralized. The leaving Ar atom gives no long-range Coulomb potential,

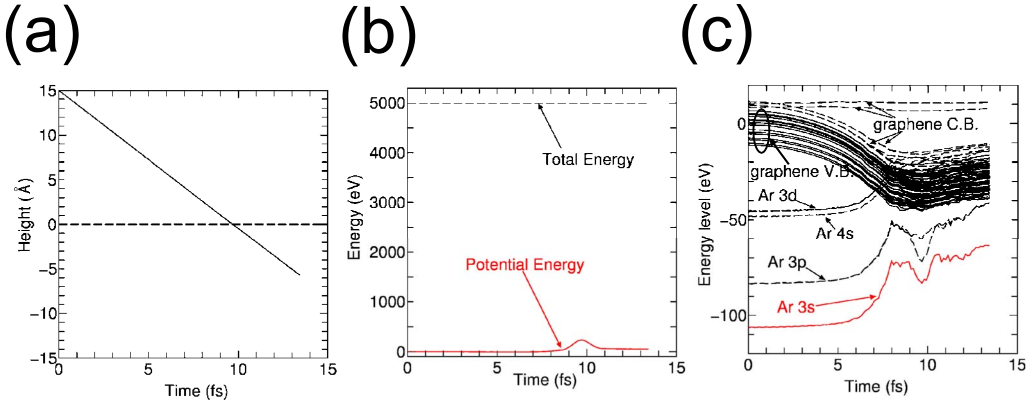

FIG. 2. (Color online) (a) Time evolution of atomic position of Ar^{7+} ion above graphene sheet with incidence kinetic energy of 5 keV, with 0 Å as the level of the sheet. (b) Corresponding potential energy in red (dark gray) and total energy (potential energy plus kinetic energies of all ions) as a function of time, showing the energy conservation rule. (c) Corresponding expectation values of the system. Graphene valence and conduction bands are denoted by solid and dotted lines; Ar $3s$ in red (dark gray) and other levels are also denoted by solid and dotted lines. Note that all dotted lines represent empty states and that higher Rydberg states of Ar are not displayed.

and a positive charge remains in the graphene sheet. Therefore, all energy levels related to the graphene sheet should remain at the lower values. However, the calculation shows a restoration in the energy levels of the graphene-related bands. This suggests that the leaving Ar ion retains some positive charge although the Coulomb potential of the ion becomes weaker and weaker as it leaves. This behavior can be attributed to partial neutralization of the ion when it passes through the graphene sheet. We determined that, at the final position shown in Fig. 2(a), the integrated valence charge density is 6.89 electrons around the Ar nucleus within a radius of 2.65 Å. Although the charge transfer is incomplete, a significant increase in the Ar atomic levels is seen, which is, of course, due to the increase in charge density around the Ar nucleus.

As mentioned, some of the conduction bands were only weakly affected by the passing of the Ar^{7+} ion through the graphene sheet. This is due to the extended nature of the wave functions of these bands. In fact, these wave functions constitute a family of interlayer states of stacked graphene sheets.[19]

Finally, we mention another practical technique for treating the very high incidence energy of ions. Under certain experimental conditions, the generated ions are not deaccelerated by the retarding grid, resulting in very high incident kinetic energies. For an Ar^{7+} ion, as an example, the kinetic energy ranges from a few hundred keV to MeV.[20] Given such high kinetic energy, the ion velocity should be comparable to the Fermi velocity of electrons, and thus, the Born-Oppenheimer approximation does not hold.[11]

When we imparted a sudden velocity to ions with very high kinetic energy, the TDDFT-MD simulation induced an electronic excitation. Figure 3 shows the simulation results for an Ar^{7+} ion with a suddenly applied kinetic energy of 500 keV. The time evolution of the expectation values of the atomic orbitals is shown in Fig. 3(a). Although the empty levels are not exactly representative of the exact excited states of the Ar^{7+} ion, they have the same characteristics, so projection of these empty states can be taken as an approximated measure of orbital excitation. Since the ion velocity was ten times that in the previous simulation (Fig. 2), smaller Δt (1.815×10^{-4} fs) was used. The calculated results obviously show significant oscillation (20 eV amplitude) of the expectation values. This oscillation was initiated by the sudden replacement of a high-velocity Ar^{7+} ion that could not be immediately followed by electron wave functions at the beginning of the TDDFT simulation. The oscillation remains as the solution of the time-dependent Schrödinger equation unless quantum decoherence occurs. In the TDDFT-MD simulation, we monitored the time evolution of the overlap between the original Ar $3s$ orbital and several Ar pseudorbitals used in the present pseudopotentials[17] and found that the original Ar $3s$ orbital contained $3p$ and $3d$ components. This means that the simulation induced intra-atom excitation.

To minimize this intra-atom electronic excitation without interaction with the target, we tested the effect of gradual ion acceleration by adding a fictitious external potential, $V_{ext}(R_Z)$, to the Ar ion:

$$V_{ext}(R_Z) = E\left(\frac{2}{\pi}\right)\tan^{-1}\left(\frac{R_Z - 15.0\ \text{Å}}{10\ \text{Å}}\right), \tag{5}$$

where R_Z is the height of the Ar^{7+} ion. We set E to 500×1.3 keV. (When a graphene sheet is included, $R_Z=0$ Å should correspond to the height of the sheet.)

With this fictitious parameter, the Ar^{7+} ion is first located at $R_Z=15$ Å and then reaches a high velocity with a corresponding kinetic energy of over 500 keV at around 1.4 fs, see inset in Fig. 3(b), corresponding to $R_Z=0$ Å. With this gradual acceleration scheme, the oscillation of the expectation values was significantly reduced [Fig. 3(b)], and the original Ar $3s$ orbital retained its characteristics. We are using this fictitious potential to investigate the interaction of very fast Ar^{7+} ions and a graphene sheet, but the calculations are very time consuming since Δt is extremely small, as mentioned above. The results will be presented elsewhere.

In summary, we demonstrated a technique using real-time TDDFT and MD simulation[8] for investigating the interaction

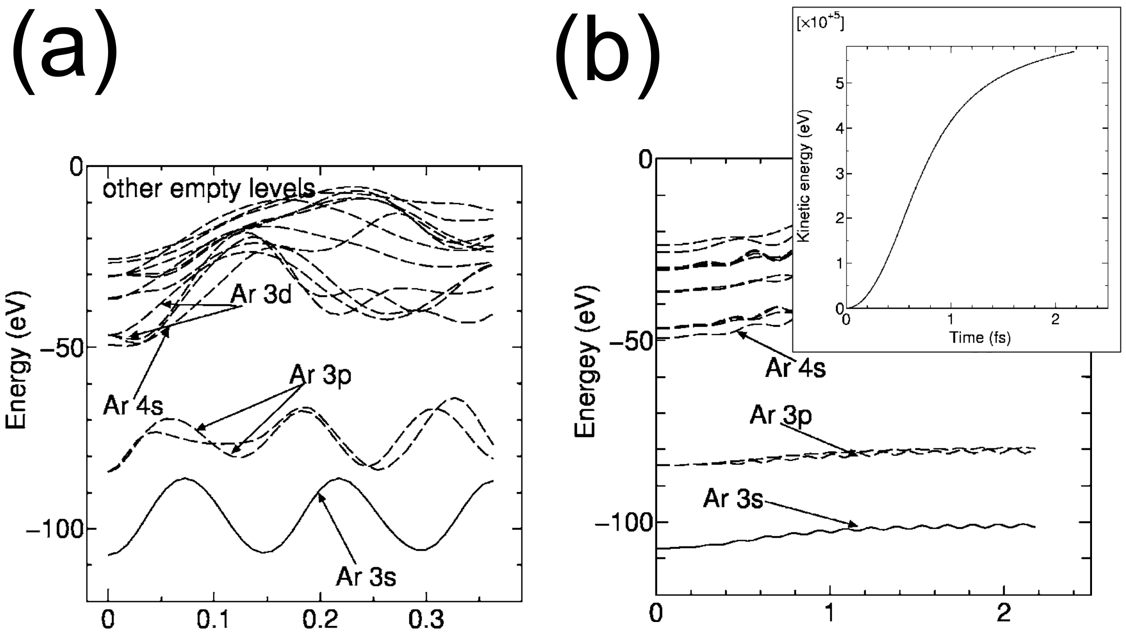

FIG. 3. (a) Time evolution of atomic orbital of Ar^{7+} ion with sudden initial velocity corresponding to kinetic energy of 500 keV. (b) Corresponding plot with gradual acceleration as illustrated in inset, which is the time evolution of the ion's kinetic energy.

between colliding charged materials, in which the dynamics of the charge transfer plays a key role in addition to that of the ion-ion interactions. The electron dynamics was investigated within the framework of TDDFT-MD simulation using superimposed electronic structures of individual systems as the initial condition. With this simulation technique, the interactions caused by an Ar^{7+} ion passing through a graphene sheet can be calculated with numerical stability, as proven by the conservation of total energy. Furthermore, the use of a fictitious potential to gradually accelerate the ion up to high kinetic energy minimizes intra-atomic orbital excitation unless the ion interacts with a solid surface. These techniques are approximate but practical, and useful for future investigation of the interactions of high-speed ions with condensed matters.

We would like to point out that the dynamics of charge transfer is a complicated many-body problem, so it is important to consider the proper functional forms of DFT or inclusion of two-electron Auger process if one is to compare the computed charge transferred to penetrated ion with those available for experiments in detail.

All calculations were performed using the SR1100 System in the Supercomputer Center of the Institute of Molecular Science and using the SX8 System at the NEC Fuchu Plant. Y.M. is supported by the Next Generation Supercomputer Project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan. H.Z. is supported by NSAF 10676025, China.

---

[1] S. Matsui, Proc. IEEE **85**, 629 (1997).

[2] T. Meguro, A. Hida, M. Suzuki, Y. Koguchi, H. Takai, Y. Yamamoto, K. Maeda, and Y. Aoyagi, Appl. Phys. Lett. **79**, 3866 (2001).

[3] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[5] N. Nakaoka, K. Tada, S. Watanabe, H. Fujita, and K. Watanabe, Phys. Rev. Lett. **86**, 540 (2001).

[6] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[7] P. Ehrenfest, Z. Phys. **45**, 455 (1927).

[8] O. Sugino and Y. Miyamoto, Phys. Rev. B **59**, 2579 (1999); **66**, 089901(E) (2002).

[9] K. J. Schafer, N.-H. Kwong, and J. D. Garcia, Surf. Sci. **199**, 132 (1988).

[10] C. Lemell, X.-M. Tong, K. Tőkesi, L. Wirtz, and J. Burgdörfer, Nucl. Instrum. Methods Phys. Res. B **235**, 425 (2005).

[11] A. V. Krasheninnikov, Y. Miyamoto, and D. Tománek, Phys. Rev. Lett. **99**, 016104 (2007).

[12] Y. Miyamoto, Appl. Phys. Lett. **91**, 113120 (2007).

[13] If we include the forces from nearest neighbor cells and assume no screening, the total force should be as follows:

$$F = z^2e^2\left\{\frac{1}{(L+d)^2} - \frac{1}{(L-d)^2}\right\} = -4z^2e^2\left\{\frac{d/L^3}{\left(1+\dfrac{d}{L}\right)^2\left(1-\dfrac{d}{L}\right)^2}\right\}.$$

Here, L is the period of the supercell in the surface-normal direction, and d is the distance from an ion in a primitive supercell. It shows that if L is long enough, the error of force is marginal.

[14] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[15] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[16] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[17] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[18] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[19] See, for example, H. Kamimura, Phys. Today **40** (12), 64 (1987).

[20] S. Bashkin, H. Oona, and E. Veje, Phys. Rev. A **25**, 417 (1982).