

Time-dependent density functional molecular dynamics simulation

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We present a scheme to simulate the coupled electron-ion dynamics within the density functional theory. In our scheme, letting the electrons and ions follow the time-dependent Kohn-Sham equation and the Newton equation, respectively, ultrafast dynamics induced by electronic excitation is investigated. We first show approximations made in that simulation to clarify the advantage and limitation of this scheme. Since the simulation is quite numerically unstable, we show techniques to overcome the difficulty. Finally, we present several applications to realistic materials: clusters, surfaces, and defects.

Electron-ion dynamics within the time-dependent DFT simulation

Chemical reaction triggered by electronic excitation has received much interest recently. Electron-ion dynamics simulation in intense laser field was one of the central topics of the present symposium.¹⁾ In spite of the recent progress made in the numerical algorithms, it is still difficult to include all the many-body correlation effect when more than two electrons exist. In this context, it is important to establish approximated simulation method within the density functional theory (DFT) or molecular orbital theory. The aim of the present paper is to elucidate one of such simulations: coupled Newton equation for ions and time-dependent Schrödinger (Kohn-Sham) equation for electrons,

$$M \frac{d^2 \mathbf{R}}{dt^2} = - \frac{\partial V}{\partial \mathbf{r}} \quad (1)$$

$$i \frac{\partial \Psi(\mathbf{r})}{\partial t} = H_{DFT} \Psi(\mathbf{r}). \quad (2)$$

The coupled equation can be recognized as an extension of the *ab initio* molecular dynamics simulation to allow an investigation of the dynamics of the electrons also. In particular, when the pseudo-crossing point is passed, one can monitor the way the electrons begin to have amplitude on both potential energy surfaces. The adiabaticity of the dynamics can thus be investigated.

Because of the approximations made in the coupled equation, one needs caution when performing the TD-DFT MD simulation. One approximation is on the exchange-correlation potential V_{XC} . Unlike the time-independent case, the potential depends on the charge density in the past and appropriate functional form for V_{XC} has not been found yet. In this context, one has to adopt the functional developed for time-independent case. Although there are a few examples in which such functional gives reasonable description,²⁾ the limitation is not known yet.

The coupled equation also approximately describes the system using only one wavefunction for electrons and one function for ions. Such treatment neglects the many-body coupling between the electrons and ions typically appears in the vibronic state. It is known that more than one function is essential to describe the system when significant non-adiabatic

transition occurs. Therefore the simulation cannot be continued beyond the non-adiabatic transition unless more elaborate procedure such as the surface hopping³⁾ is adopted. We show below several examples where the TD-DFT MD simulation, in spite of that limitation, is effective in getting information concerning how fast the non-transition begins to occur and to which potential energy surfaces the system transfers.

How to solve the coupled equation

When solving the coupled equation, the Suzuki-Trotter type split operator method⁴⁾ is most appropriate in our case, because the method is unconditionally stable, keeps unitarity of the time-evolution operator, and can be applied even when the potential explicitly depends on time. The last reason is especially important when the potential is determined self-consistently and thus has significant time-dependence.

We have found that the TD-DFT MD simulation is still numerically unstable unless the following techniques are adopted. One is to smooth the Hamiltonian by cutting off the high frequency components in reciprocal space. For this purpose, cutting off large G-components of the charge density, potential energy, and kinetic energy operators was found very effective in reducing high frequency ω -components in the wavefunction.⁵⁾ The other technique is the railway curve interpolation of the self-consistent potential, which keeps the time-reversal symmetry of the simulation. The advantage was demonstrated in our previous paper,⁵⁾ where electron dynamics in Al_2 molecule and electron-ion dynamics in photo-excited potassium trimer were simulated.

Applications

Hydrogen is known to dissociate from H-terminated Si(111) surface when stimulated by STM tip or laser pulse, but the mechanism is not very well understood yet. To simulate the hydrogen dissociation, we first selected an occupied bonding state (σ) localized around an H-Si bond and an unoccupied anti-bonding state (σ^*) localized around the same bond. Exciting one electron from σ to σ^* , self-consistent electronic state was obtained. Considering that the excited state is

created by the stimulation, we performed the TD-DFT MD simulation.⁶⁾ When a small cluster Si_4H_{10} was used as the model, the hydrogen atom was found to dissociate on the excited potential energy surface within 10 fs. When a slab was used as the model, on the other hand, the excited state mixed with the bulky extended state within 7 fs and the driving force for the dissociation was quickly reduced. Because the non-adiabatic transition took place soon after, the dynamics occurring afterward could not be investigated. However, striking difference between the cluster and the slab was clear from the simulation. Investigating the time evolution of the one-electron state, we also found that, although σ^* -hole state quickly mixed with bulky state, σ -electron did not. Such asymmetry between the unoccupied state and occupied state was also seen in the simulation where an electronically excited SiH_2 molecule was collided with $\text{Si}(111)$ surface.⁶⁾

The dynamics of Si-H complex in GaAs behaves differently from that at the Si surface.⁷⁾ The excited electronic state localized near the Si-H complex was found very stable against the non-adiabatic transition. The dynamics continued on the excited potential surface at least for sub picosecond. When the simulation started by giving initial velocity to the hydrogen, the hydrogen was found to dissociate from the Si. From such simulations we estimate that the potential barrier for the dissociation is smaller than 0.2 eV, which is much smaller than the barrier along the ground state potential energy surface, 1.8 eV. This result indicates that electronic excitation is an effective way to let the hydrogen dissociate.

With the TD-DFT MD simulation, it is also possible to simulate the electron dynamics applying a uniform electric field. This is a way to investigate the electric properties of materials. As a very simple demonstration, we performed the

simulation for a 1D array of Al atoms. By continuing the simulation until an equilibration is realized, we could obtain how the resistance depends on the applied electric field. The resistance showed a maximum when the energy obtained from the electric field by hopping between two Al atoms becomes comparable to the excitation energy of the array. Application to larger system is currently done.

Future target

As has been explained above, the TD-DFT MD simulation is a practical approximate way to investigate the electron-ion dynamics. The most attractive aspect is the applicability to large complex systems. The accuracy is not known however. To establish the method, we must improve the exchange-correlation functional, properly describe the many-body correlation between electrons and ions, and include the quantum effect of the ions. Such work will greatly extend the applicability of the density functional theory.

References

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