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Ehrenfest Molecular Dynamics for Quantum Process under Ion Injection onto Solid Surfaces and Seed Coats

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In the fields of plasma application and fusion science, atomic-level simulations have been employed to elucidate plasma-material interaction. As the focus of research has broadened from sputtering processes to chemical reaction processes, the simulation methods commonly used have correspondingly evolved from the binary collision approximation (BCA) to molecular dynamics (MD) and density functional theory (DFT). However, an unsolved theoretical problem is that these calculation methods cannot handle charged particles directly due to model limitations, and in most cases the incident ions are replaced by neutral atoms. In the case of BCA and MD, it is due to interaction potentials assuming neutral atoms. On the other hand, in the case of DFT, it is due to the limitation that the possible solutions of the electron wave function are restricted to the ground state only.

Therefore, recently, we have been developing a new code QUMASUN[1] to implement the Ehrenfest molecular dynamics[2]. This method hybridizes the Newton's equations of motion for nuclei as classic particles and the time-dependent Kohn-Sham equation for electronic wave function according to time-dependent density functional theory (TDDFT).

The term "TDDFT" can be broadly categorized into real-time TDDFT and linear-response TDDFT. In the QUMASUN code, the former real-time TDDFT is adopted to handle the motion of nuclei. Electronic orbitals are represented as fields on a real-space grid. However, by employing a pseudopotential method, the inner core electrons are treated within the frozen-core approximation, and only the valence electrons are explicitly computed. As for the actual pseudopotential data, the Vanderbilt type pseudopotential[3] is used. Actually, the Optimized Norm-Conserving Vanderbilt (ONCV) model[4,5] and Morrison-Bylander-Kleinman (MBK) model[6] are supported.

From the viewpoint of computational resources, the self-consistent field (SCF) DFT calculations for obtaining the ground state require a computational cost scaling as $O(N^3)$. In contrast, real-time TDDFT and Ehrenfest MD simulations benefit from the real-space grid representation of the wavefunctions, leading to computational costs of $O(N^2)$ or $O(N^2 \log N)$. As a result, although Ehrenfest MD requires a time step that is roughly 1/100 of that used in Born–Oppenheimer (BO) molecular dynamics, where forces are obtained via SCF-DFT at each step, the overall computation remains feasible within practical time scales. Specifically, with computing resources on the order of a few hundred CPU cores, each simulation step can be completed in under one second. Therefore, despite using a small physical time step ($\Delta t \approx 1–5 \times 10^{-19}$ s), it is sufficiently feasible to demonstrate the interaction process between plasma ions and surfaces over a span of one to several days.

By using the QUMASUN code, it was possible to reproduce the quantum transitions process of electrons from solid surface to incoming ions, which are explicitly treated as charged particles. Actually, neutralization processes of hydrogen ion[7] and helium-ion[1] on tungsten surfaces were simulated. Simulations of hydrogen and helium ions reflected from a tungsten surface at an incident energy of 100 eV revealed that the outgoing ions exist in a quantum superposition of different charge states. In the case of hydrogen[7], a single simulation produces a state that includes H^+ (positive ion), H^0 (neutral atom), and H^- (negative ion) simultaneously. By analyzing this wavefunction, the detection probabilities for each charge state can be quantitatively estimated. These results suggest that, upon measurement in a plasma experiment, the quantum state probabilistically collapses into one of the discrete charge states, consistent with the probabilistic nature of quantum measurement.

Similar quantum phenomena, where plasma-derived particles evolve into superposition states through interactions with material, may arise in other systems as well. As an example, we examine the interaction between neutral radical molecules generated by plasma and the surface of plant seed coats. Our simulations indicate that NO_x radicals, upon interacting with cellulose molecules which is a primary constituent of the seed surface, can probabilistically shift into anionic or cationic states without undergoing chemical reactions. These findings open up a new frontier in exploring quantum processes driven by plasma–material interactions.

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