

Correlated electron-ion dynamics in metallic systems

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Abstract

In this paper we briefly discuss the problem of simulating non-adiabatic processes in systems that are usefully modelled using molecular dynamics. In particular we address the problems associated with metals, and describe two methods that can be applied: the Ehrenfest approximation and correlated electron-ion dynamics (CEID). The Ehrenfest approximation is used to successfully describe the friction force experienced by an energetic particle passing through a crystal, but is unable to describe the heating of a wire by an electric current. CEID restores the proper heating.

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1. Non-adiabatic processes

Non-adiabatic processes, as the name suggests, can be defined by the failure of a particular approximation (the adiabatic approximation). In this approximation, which is very often extremely successful, the electrons are assumed to follow the nuclei in such a way that they are always in an eigenstate associated with the instantaneous positions of the nuclei which are seen as merely providing an external potential. That is, the electrons appear to be in some sense clamped to the nuclei. This then can be used to define a set of fixed energy surfaces corresponding to the positions of the nuclei and to the degree of excitation of the electrons. Non-adiabatic processes can then be thought of as those

in which the system makes transitions between the adiabatic energy surfaces.

The transitions between the energy surfaces can take place because the nuclei move too quickly for the electrons to adapt fully to the new environment generated by the displaced nuclei. This is encountered during electron transfer reactions in which the rate at which electrons move between two sites is very low, so that they remain trapped on one site even though the nuclei would like to drag them over to another.

These processes are generally important when electrons and nuclei are mutually out of equilibrium [1], in which case non-adiabatic processes work to restore equilibrium. This can be observed, for example, in the heating of wires by an electric current, or the response of electrons in a metal to a fast projectile.

Because non-adiabatic processes are often a weak correction to an underlying adiabatic process, they can be

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often successfully treated using perturbation theory. For example, in the heating of a wire the process of the exchange of energy between the electrons and the nuclei is a small correction on the steady flow of the electric current [2,3]. On the other hand, when we wish to study complex systems, or where we are interested in the dynamics, molecular dynamics (MD) is extremely useful. Thus there is an incentive to produce MD schemes that incorporate non-adiabatic effects.

2. Ehrenfest dynamics and surface hopping

Molecular dynamics is a simple, but remarkably powerful, modelling technique. In it, atoms are treated as classical particles that obey Newton's laws of motion. These particles then interact with one another by force laws. In more sophisticated treatments these force laws can be derived from an explicit treatment of the electrons. While very flexible, this approach is usually limited to adiabatic phenomena. The introduction of non-adiabatic processes in fact involves a major revision of the theory.

A number of very ingenious methods for introducing non-adiabatic processes into MD have been proposed [1]. Here we just mention two of them because of their popularity and their obvious connection with conventional MD. They also are representative of two broad categories of method, and by comparing them we discover the advantages of each category. The methods are the Ehrenfest approximation (in which the dynamics are continuous, and no knowledge of electron surfaces is required beforehand) and surface hopping (in which energy surfaces and transitions between them are treated explicitly) [4–10]. In both cases, the nuclei are treated as classical particles that obey Newton's laws. Thus they evolve according to

$$\dot{R} = P/M \quad (1)$$

$$\dot{P} = F = -\frac{\partial V_{\text{NN}}}{\partial R} - \int \frac{\partial V_{\text{eN}}}{\partial R} \rho_e(r) dr \quad (2)$$

where R is a nuclear position, P is the corresponding momentum, M is the mass of the nucleus, and V_{NN} and V_{eN} are the nucleus–nucleus and electron–nucleus interactions. ρ_e is the electron density, and is found from the electron wavefunction Φ using

$$\rho_e(r) = N \int |\Phi(r, r_2 \dots r_N)|^2 dr_2 \dots dr_N \quad (3)$$

where N the number of electrons. The difference between the two methods is in the scheme used to compute the evolution of the electrons. In the Ehrenfest approximation, the electron wavefunction is obtained from the time-dependent Schrödinger equation

$$i\hbar\dot{\Phi} = \hat{H}_e(R)\Phi \quad (4)$$

where $\hat{H}_e(R)$ is the Hamiltonian for the electrons. For surface hopping the electronic state is found from the time independent Schrödinger equation

$$\hat{H}_e(R)\Phi = E(R)\Phi \quad (5)$$

In both cases R refers to the instantaneous position of the nuclei. Because the nuclei move they introduce a time dependence into the evolution of the electrons. If nothing further were done, then surface hopping would reduce to the adiabatic approximation, where the electrons remain always in a given state that follows the nuclei instantaneously. However, when the nuclei move to a position at which two energy surfaces are close in value, then a hop between those surfaces is permitted with finite probability. If the hop succeeds, the nuclei continue to move on the new surface until a new transition is allowed.

A key practical difference between these two methods is that for surface hopping you need to know what the energy surfaces are, whereas they are sampled automatically by the Ehrenfest approximation. This is important in metallic systems where the surfaces are closely spaced, and it is thus hard to keep track of them, and is not even clear if one surface alone is being sampled by the moving nuclei. Thus, for metallic systems Ehrenfest appears very attractive. We note in passing, that there is a modified version of surface hopping that has been applied to systems with continuous distributions of levels [10]. However, it is not widely used.

Unfortunately, the Ehrenfest approximation does not reproduce all transitions between surfaces properly (surface hopping is often considerably better). This is a consequence of the fact that the nuclei only see the average smoothed out density of the electrons instead of experiencing scattering by individual particles. This is clear from Eq. (2) where we see that the force on the nuclei depends only on the electron density.

Thus the two main schemes that are straightforward extensions of MD do not provide the functionality that we seek. Correlated electron-ion dynamics is a scheme for correcting the Ehrenfest method to restore the full electron-nuclear interactions in a systematic way, while holding onto the ability to study metals in a straightforward manner. Before we discuss this approach we consider some work we have done in which the Ehrenfest approximation has been very successful, and some other work in which it gives incorrect answers.

3. Application of Ehrenfest dynamics

3.1. Success: radiation damage

The successful application is of the drag force on a fast ion produced by the electrons as it passes through a crystal. This is an important effect in several situations, though the motivation in this case is the desire to understand the damage caused by fast neutrons to the structures that surround the plasma in a hydrogen fusion power plant. The hydrogen fuel with the lowest ignition temperature (4.5×10^7 K) is a mixture of deuterium and tritium. The energy producing reaction is $D + T \rightarrow He + n$. The helium nucleus and neutron have energies of 3.5 and 14.1 MeV,

respectively. When the neutron collides with the wall of the blanket around the plasma it kicks out an atom which could acquire an energy as high as 1.9 MeV. It is this ion that experiences the drag force.

In our simulation we studied a relatively low energy particle (2 keV). We start with a box of 2016 stationary copper atoms with periodic boundary conditions. To this we add an additional atom in a tetrahedral interstice. The electrons are described by a simple tight binding model with a single s -type orbital on each atom [11]. The initial electron state is the lowest free energy state for a canonical electron temperature of 1000 K. Charge self-consistency is treated locally to each site through a Hubbard- U term ($U = 7$ eV). At time $t = 0$ the interstitial is given a kick of 2 keV in the $[1\ 0\ 0]$ direction. Then a 180 fs simulation is performed in the Ehrenfest approximation using the program ICED (imperial college Ehrenfest dynamics), with a time step of 0.05 fs.

The simulation was analysed by monitoring several quantities. At regular intervals we computed the difference between two energies (ΔE): that generated by the Ehrenfest simulation and that obtained by finding the Born–Oppenheimer energy (the electronic internal energy at the canonical temperature of 1000 K) corresponding to the instantaneous nuclear positions. This gives a measure of the non-adiabatic heating of the electrons which produces the drag force on the fast moving atoms. We also observed the charge redistribution amongst the atoms. We find that there is a propagating front that is depleted of electrons, with the resulting excess electrons accumulating in the wake of the incident particle.

We find that the excess electron energy (ΔE) grows linearly with time at about 0.4 eV/fs (see Fig. 1). This is consistent with the usual expression for the viscous drag force ($F_{\text{drag}} = -\gamma\dot{R}$) which results in the power provided by the ions to the electrons ($-F_{\text{drag}}\dot{R}$) being equal to $\gamma\dot{R}^2$, which is proportional to the total kinetic energy of the atoms. As the fraction of the total energy transferred to the electrons is small, the average kinetic energy of the atoms

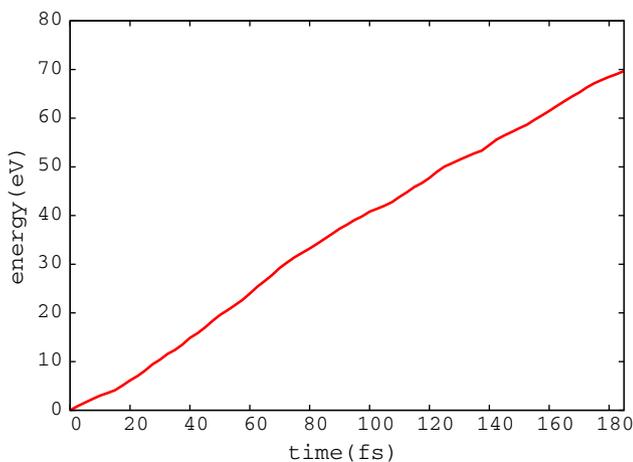


Fig. 1. The variation of the increase in electronic energy with time during the course of the simulation.

can be treated as roughly constant, and hence we have a constant rate of power supply to the electrons.

As the interstitial passes neighbouring atoms, the neighbours are kicked off their lattice sites. These neighbours then collide with their neighbours. A parabolic positively charged wavefront of displaced atoms is formed as the interstitial slows (see Fig. 2).

These simulations are successful as the process that is suppressed by the Ehrenfest approximation (the spontaneous emission of phonons by excited electrons) is not important for the friction forces. However, for the Joule heating of a wire by an electric current this is the most important process.

3.2. Failure: Joule heating

The simulation of heating in nanowires by Ehrenfest dynamics has been described in detail elsewhere [12,13], and only a very brief summary is given here. The simulations were of a wire one atom thick, with the electrons described by a simple tight binding model with one s -orbital per atom. Open boundaries were used to allow a current flow, with the two leads offset by a given voltage. One atom in the middle of the wire was permitted to move, and its kinetic energy was monitored as a function of time (see Fig. 3). It was given an initial kinetic energy corresponding to 400 K. We found that at small biases (below 1 V) the atom cooled down, but for high voltages it heated up. This is qualitatively correct, except that the threshold voltage should be about the quantum of vibration of the central atom (0.05 V) instead of 1 V as observed. So, to model heating in a wire we clearly need an improved scheme.

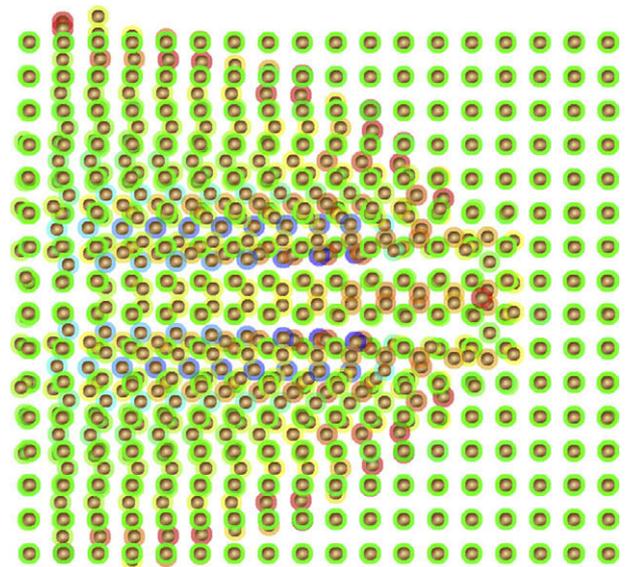


Fig. 2. A snapshot of the atoms at 75 fs. The interstitial started at the left of the picture. The red coloured atoms are positively charged, while the blue coloured atoms are negatively charged. Note the front does not have a positive and negative charged side, rather electrons are pushed out into the bulk faster than the speed of the front. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

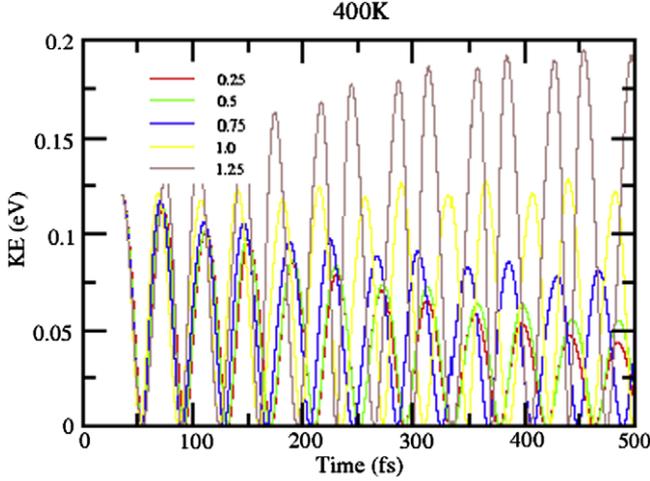


Fig. 3. This plot shows the variation in the kinetic energy of the mobile atom at the centre of the wire as a function of time and applied bias. For low voltages (below 1 V) we see that the amplitude of oscillation of the atom decreases over time, whereas for sufficiently high voltages (above 1 V) it increases slowly. Note that the voltage at which we find the onset of heating is much too large: it should be of the order of the quantum of vibration of the atom which is about 0.05 eV.

4. Correlated electron-ion dynamics

To obtain the correct heating we need to relax the mean field approximation used in Ehrenfest dynamics. However, we wish to retain the classical structure of the nuclear dynamics, so we start from the exact Ehrenfest equations (not to be confused with the approximation) which are

$$\dot{\bar{R}} = \bar{P}/M \quad (6)$$

$$\dot{\bar{P}} = \bar{F} = -Tr \left\{ \frac{\partial \hat{H}}{\partial \bar{R}} \hat{\rho} \right\} \quad (7)$$

where now \bar{R} and \bar{P} are the average positions and momenta of the nuclei, \hat{H} is the complete Hamiltonian for the combined system of electrons and nuclei, and $\hat{\rho}$ is the corresponding density matrix. The trace (Tr) is simply the integral over all electronic and nuclear coordinates. The density matrix is found from the wavefunction $\Psi(Rr)$ using $\rho(Rr, R'r') = \Psi(Rr)\Psi^*(R'r')$ where R is a nuclear coordinate and r is an electronic coordinate.

The difference between Eqs. (7) and (2) is that the wavefunction in Eq. (7) is for both electrons and nuclei, and not just for electrons. We now make the key approximation, namely that the nuclear wavefunctions are localised about the mean position \bar{R} . This enables us to make a Taylor expansion about the mean position. We write the total Hamiltonian as a sum of the nuclear kinetic energy and the remainder $\hat{H} = \hat{T}_N + \hat{H}_e(\bar{R})$, and get

$$\begin{aligned} \hat{H}_e(\hat{R}) &= \hat{H}_e(\bar{R}) + (\hat{R} - \bar{R}) \frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}} + \frac{1}{2} (\hat{R} - \bar{R}) (\hat{R} - \bar{R}) \\ &\quad \times \frac{\partial^2 \hat{H}_e(\bar{R})}{\partial \bar{R} \partial \bar{R}} + \dots \end{aligned} \quad (8)$$

Substituting Eq. (8) into Eq. (7) gives

$$\dot{\bar{P}} = -Tr_e \left\{ \hat{\rho}_e \frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}} \right\} - Tr_e \left\{ \hat{\mu} \frac{\partial^2 \hat{H}_e(\bar{R})}{\partial \bar{R} \partial \bar{R}} \right\} + \dots \quad (9)$$

where the trace is taken over electronic coordinates and

$$\begin{aligned} \hat{\rho}_e &= Tr_N \{ \hat{\rho} \} \\ \hat{\mu} &= Tr_N \{ (\hat{R} - \bar{R}) \hat{\rho} \} \\ \hat{\lambda} &= Tr_N \{ (\hat{P} - \bar{P}) \hat{\rho} \} \end{aligned} \quad (10)$$

and the trace has been taken only over nuclear coordinates. Thus the first term in Eq. (9) is just that used in the Ehrenfest approximation, and the second term corrects this by including microscopic correlations between the electrons and nuclei.

As with the Ehrenfest approximation we obtain our electronic matrices from equations of motion. We start from the quantum Liouville equation ($i\hbar\dot{\rho} = [\hat{H}, \rho]$), and by combining with Eqs. (8) and (10) we obtain

$$i\hbar\dot{\rho}_e = [\hat{H}_e(\bar{R}), \hat{\rho}_e] + \left[\frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}}, \hat{\mu} \right] + \dots \quad (11)$$

$$i\hbar\dot{\mu} = [\hat{H}_e(\bar{R}), \hat{\mu}] + \frac{\hat{\lambda}}{M} + \dots \quad (12)$$

We note two things: we see that the equation of motion for $\hat{\rho}_e$ is that for the Ehrenfest approximation plus corrections that include information about correlations; we have a hierarchy of coupled equations that needs to be truncated (there is an infinite set of equations, with only the first two shown above).

The lowest order scheme involves dropping all correlation matrices (μ , λ , etc.). This gives back the Ehrenfest approximation. The next level of approximation is to drop second order and higher correlations, so we keep $\hat{\rho}_e$, μ and λ . This produces the correct rate of heating for a cold wire, but does not include the scattering by excited nuclei. This is discussed at length in our previous work [14,15,1,16]. We just note the following conclusions drawn from the calculations. Because the nuclei are treated as quantum objects, they have two contributions to their kinetic energy. There is a classical contribution from the average momentum \bar{P} ($\bar{P}^2/2M$), and there is a quantum contribution from fluctuations about that average. The quantum contribution to the heating is much larger than the classical (indeed the small classical contribution contributes net cooling in our simulations). By adding higher order correlations we are able to compute the change in conductivity of the wire that occurs once the applied bias is sufficient to cause excitation of nuclear vibrations [17,16].

4.1. The future of CEID

In the above we have glossed over the problem of truncating the hierarchy in a robust manner. To produce a stable set of equations of motion this has to be handled with

care. Recently, the CEID formalism has been reworked to allow a systematic truncation that converges reliably to the exact answer as higher order correlations are included. The central idea is to project the nuclear degrees of freedom on to a basis set (harmonic oscillator wavefunctions), and then determine the equations of motion of the resulting expansion coefficients. The procedure is somewhat different from that described above, but the new expansion coefficients can in fact be related to the moments discussed above in a straightforward manner. This new approach has enabled us to model difficult systems with rather strong electron-phonon coupling.

5. Conclusions

Thus, in summary, a new scheme for modelling systems in which there is irreversible exchange of energy between electrons and nuclei has been presented. It builds on the success of the Ehrenfest approximation, adding to it those corrections needed to re-establish microscopic correlations between electronic and nuclear dynamics. This allows us not only to simulate processes dominated by the excitation of electrons by energetic nuclei (such as friction in radiation damage) but also processes dominated by spontaneous emission of phonons (such as Joule heating). Recent developments of the theory make it possible to study cases with strong electron-phonon interactions. This method, as it does not require explicit knowledge of Born–Oppenheimer

energy surfaces, is especially useful for metallic systems, and those with open boundaries.

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