Correlated electron–ion dynamics with open boundaries: formalism

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D R Bowler[1,2]**, Andrew P Horsfield**[2]**, Cristián G Sánchez**[3] **and Tchavdar N Todorov**[3]

[1] International Centre for Young Scientists (ICYS), NIMS, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
[2] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
[3] School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, UK

E-mail: david.bowler@ucl.ac.uk, a.horsfield@ucl.ac.uk, c.sanchez@qub.ac.uk and t.todorov@qub.ac.uk

Abstract
We extend a new formalism, which allows correlated electron–ion dynamics to be applied to the problem of open boundary conditions. We implement this at the first moment level (allowing heating of ions by electrons) and observe the expected cooling in the classical part of the ionic kinetic energy and current-induced heating in the quantum contribution. The formalism for open boundaries should be easily extended to higher moments of the correlated electron–ion fluctuations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Molecular dynamics, particularly coupled with electronic structure calculations for the energy of and force acting on the ions, has been phenomenally successful in fields as diverse as biology, chemistry and material science [1, 2]. However, this technique makes two key assumptions which are not always applicable: first, that ions are classical; second, that electrons are confined to the ground state (the Born–Oppenheimer approximation). Relaxing the Born–Oppenheimer approximation and evolving the electrons along with the ions (the Ehrenfest approximation) allows increased freedom and permits exploration of excited electronic states (when coupled with a suitable technique such as time-dependent density functional theory). Unfortunately, the Ehrenfest approximation does not allow proper transfer of energy from electrons to ions, which is important, among other effects, for producing heating of the ions by current carrying electrons [3].

A proper understanding of the interaction and evolution of excited electrons and ions is important in a number of problems, including (but not limited to) Joule heating in nanostructures, the initial stages of radiation damage and non-radiative decay of an excited molecular state. We have recently explored the failure of the Ehrenfest approximation to model correctly current-induced heating [3], which is largely due to the inability to treat correlations between electrons and ions (the ions are treated entirely classically, moving in a fluid of quantum electrons). We have since proposed a computationally affordable method for introducing these correlations, correlated electron–ion dynamics (CEID) [4], which can be systematically improved. However, the formalism was only applied to closed systems, with conduction of a nanostructure modelled over short timescales using a long wire (a valid technique until reflections off the ends reach the area of interest). In this paper, we extend a model for open boundary Ehrenfest molecular dynamics [5] to the CEID method, and apply it, within the first moment approximation, to the problem of Joule heating in a nanostructure.

2. Formalism

For convenience, we reproduce the important features of the CEID method; full details are given elsewhere [4]. The Ehrenfest approximation assumes that the ionic position operator, $\hat{R}_\nu$, can be replaced with the mean position of the ion, $\bar{R}_\nu$, thus giving classical ions. If, instead, we treat the entire system quantum mechanically and consider small fluctuations of the ionic position about its mean, we can define a quantity $\Delta \hat{R}_\nu = \hat{R}_\nu - \bar{R}_\nu$ and consider an expansion in terms of powers or moments of this quantity (and the corresponding canonical momentum fluctuation, $\Delta \hat{P}_\nu = \hat{P}_\nu - \bar{P}_\nu$). Formally, the CEID equations can be derived by starting with the density matrix for the *complete* system, $\hat{\rho}$; however, for the sake of brevity we now shift to a single electron description. We work with the electronic density matrix, $\hat{\rho}_e$, and electronic correlation operators. At the first moment level we need only consider

$$\hat{\mu}_\nu = \text{Tr}_{I,e2\ldots N}[\hat{\rho}\Delta\hat{R}_\nu] \tag{1}$$

$$\hat{\lambda}_\nu = \text{Tr}_{I,e2\ldots N}[\hat{\rho}\Delta\hat{P}_\nu], \tag{2}$$

where $\text{Tr}_{I,e2\ldots N}$ indicates that we have traced out the ionic degrees of freedom, and the degrees of freedom for all electrons apart from one.

The time dependence of the system is given by several equations: first, the usual Ehrenfest equations $\dot{\bar{R}}_\nu = \bar{P}_\nu/M_\nu$ and $\dot{\bar{P}}_\nu = \bar{F}_\nu$; second, the equation for the forces at the first moment level,

$$\bar{F}_\nu = \hat{F}_\nu^{(0)} + \text{Tr}_{e,1}\{\hat{\rho}_e\hat{F}_\nu\} - \sum_{\nu'}\text{Tr}_{e,1}\{\hat{\mu}_{\nu'}\hat{K}_{\nu'\nu}\}, \tag{3}$$

where $\hat{F}_\nu^{(0)}$ is a scalar term originating from the interaction between ions, and is independent of the electronic degrees of freedom; finally, the time evolution of a general electronic operator $\hat{q}_\nu$, which is given by

$$i\hbar\frac{\partial \hat{q}_\nu}{\partial t} = [\hat{H}, \hat{q}_\nu] + i\hbar\hat{D}_\nu^q, \tag{4}$$

where $\hat{D}_\nu^q$ is a driving term of some kind. Within the Hartree–Fock approximation, specific examples of $\hat{D}_\nu^q$ for the density matrix, and the first moments of the ionic position and momentum, are given by [4]

$$\hat{D}^\rho = -\frac{1}{i\hbar}\sum_\nu[\hat{F}_\nu, \hat{\mu}_\nu] \tag{5}$$

$$\hat{D}_{\nu}^{\mu} = \frac{\hat{\bar{\lambda}}_{\nu}}{M_{\nu}} \tag{6}$$

$$\hat{D}_{\nu}^{\lambda} = -\sum_{\nu'} \bar{K}_{\nu\nu'} \hat{\mu}_{\nu'} - \hat{\rho}_e \hat{F}_{\nu} \hat{\rho}_e + \tfrac{1}{2}(\hat{F}_{\nu} \hat{\rho}_e + \hat{\rho}_e \hat{F}_{\nu})$$

$$+ \sum_{\nu'} (\hat{\mu}_{\nu'} \hat{K}_{\nu\nu'} \hat{\rho}_e + \hat{\rho}_e \hat{K}_{\nu\nu'} \hat{\mu}_{\nu'}) - \tfrac{1}{2} \sum_{\nu'} (\hat{K}_{\nu\nu'} \hat{\mu}_{\nu'} + \hat{\mu}_{\nu'} \hat{K}_{\nu\nu'}), \tag{7}$$

where ν is the index of a *moving* ion, M_{ν} is its mass, $\hat{F}_{\nu} = -\partial \hat{H}(\bar{R})/\partial \bar{R}_{\nu}$ is the force operator on the ion, $\hat{K}_{\nu\nu'} = \partial^2 \hat{H}(\bar{R})/\partial \bar{R}_{\nu} \bar{R}_{\nu'}$ is a generalized spring constant and $\bar{K}_{\nu\nu'} = \hat{K}_{\nu\nu'}^{(0)} + \mathrm{Tr}_e\{\hat{\rho}_e \hat{K}_{\nu\nu'}\}$, which includes a contribution from the scalar pair potential ($\hat{K}_{\nu\nu'}^{(0)}$). It is important to note that the time evolution of all electronic–ionic correlation operators (for all levels of moment expansion) can be written in this way.

2.1. Open boundaries

We turn now to the problem of open boundary conditions (see, for instance, [6]). We wish to study the behaviour of a system consisting of ions and electrons which is free to exchange energy and particles (at present only electrons) with the environment. We do this by extending our earlier, open boundary Ehrenfest formalism [5]. We divide the system of interest into two areas: the device (where the interesting physical problems are located, given by subscript D) and the environment (which represents a large, external area notated E, for instance leads connected to a nanojunction). We can partition the time evolution for a general operator, equation (4), into three different equations (dropping the subscript ν for convenience):

$$i\hbar \frac{\partial \hat{q}_{\mathrm{D}}}{\partial t} = [\hat{H}_{\mathrm{D}}, \hat{q}_{\mathrm{D}}] + (\hat{H}_{\mathrm{DE}} \hat{q}_{\mathrm{ED}} - \hat{q}_{\mathrm{DE}} \hat{H}_{\mathrm{ED}}) + i\hbar \hat{D}_{\mathrm{D}}^{q} \tag{8}$$

$$i\hbar \frac{\partial \hat{q}_{\mathrm{DE}}}{\partial t} = \hat{H}_{\mathrm{D}} \hat{q}_{\mathrm{DE}} - \hat{q}_{\mathrm{D}} \hat{H}_{\mathrm{DE}} + \hat{H}_{\mathrm{DE}} \hat{q}_{\mathrm{E}} - \hat{q}_{\mathrm{DE}} \hat{H}_{\mathrm{E}} + i\hbar \hat{D}_{\mathrm{DE}}^{q} \tag{9}$$

$$i\hbar \frac{\partial \hat{q}_{\mathrm{E}}}{\partial t} = [\hat{H}_{\mathrm{E}}, \hat{q}_{\mathrm{E}}] + (\hat{H}_{\mathrm{ED}} \hat{q}_{\mathrm{DE}} - \hat{q}_{\mathrm{ED}} \hat{H}_{\mathrm{DE}}) + i\hbar \hat{D}_{\mathrm{E}}^{q} - 2i\hbar \Gamma_{\mathrm{E}}(\hat{q}_{\mathrm{E}} - \hat{q}_{\mathrm{ref}}), \tag{10}$$

where we have introduced a damping term for the environment in equation (10) which will be discussed later.

As in our previous work with the density matrix [5], we seek a closed form for the time integral of the environment terms; to do so, we assume that the Hamiltonian in the environment is time independent. If we define a driving term $i\hbar \hat{G}_{\mathrm{E}} = (\hat{H}_{\mathrm{ED}} \hat{q}_{\mathrm{DE}} - \hat{q}_{\mathrm{ED}} \hat{H}_{\mathrm{DE}}) + i\hbar \hat{D}_{\mathrm{E}}$ and define the value of the *reference* driving term by $0 = [\hat{H}_{\mathrm{E}}, \hat{q}_{\mathrm{E}}(0)] + i\hbar \hat{G}_{\mathrm{E}}^{(0)} - 2i\hbar \Gamma(\hat{q}_{\mathrm{E}}(0) - \hat{q}_{\mathrm{ref}})$, then, following standard quantum mechanics (e.g. section 4.4 of [7]), we find

$$\hat{q}_{\mathrm{E}}(t) = \hat{q}_{\mathrm{E}}(0) + \int_0^t \mathrm{d}x \, \hat{O}(x)(\hat{G}_{\mathrm{E}}(t-x) - \hat{G}_{\mathrm{E}}^{(0)})\hat{O}^{\dagger}(x), \tag{11}$$

where $\hat{O}(t) = \mathrm{e}^{-\Gamma_{\mathrm{E}} t} \mathrm{e}^{\hat{H}_{\mathrm{E}} t/i\hbar}$ is a time evolution operator which arises from the commutator of $\hat{q}_{\mathrm{E}}$ and $\hat{H}_{\mathrm{E}}$ in equation (10), and includes the damping introduced in that equation. The effect of this scattering-like Γ_{E} term will be to localize $q_{\mathrm{E}}(t)$ in time.

The time evolution operators are most easily evaluated from the electronic Green functions for the environment region, $\hat{g}(z)$:

$$\hat{O}(t) = \mathrm{e}^{-\Gamma_{\mathrm{E}} t} \int \mathrm{d}E \, \mathrm{e}^{Et/i\hbar} \lim_{\eta \to 0^+} \left(-\frac{1}{\pi}\right) \mathrm{Im} \, \hat{g}(E + i\eta). \tag{12}$$

Clearly, for computational reasons, we can only treat a finite number of atoms in the environment explicitly. However, since the time evolution operators have a closed form, it

is possible for them to represent infinite or semi-infinite systems, should this be appropriate for the problem we are modelling. In the case of a nanojunction considered in this paper, the environment should be semi-infinite leads, for which we can evaluate the Green functions explicitly. Thus we implicitly include the Hamiltonian for a semi-infinite system in our finite system. If the reference operator ($\hat{q}_{\text{ref}}$ in $\hat{G}_{\text{E}}^{(0)}$ in equation (11)) is also chosen for a similar system (i.e. the implicit system in the time evolution operators) then there will be a restoring force in the environment towards the semi-infinite or infinite system value whatever the actual size of the explicit environment. This is the key part of our open boundary formalism. The main assumption underlying this is that the link between the device and the environment is short ranged: in particular, that the leads are larger than this range. This assumption will be examined in detail below.

By contrast, we cannot find such a closed solution for the device and device–environment terms, which we evolve directly using the leapfrog approximation ($f(t + \Delta t) \approx f(t - \Delta t) + 2\Delta t f'(t)$); this is unitary and time reversible, but has numerical implications which will be considered below in section 3.2.

We note that the traces of the time derivatives of the first moment operators are zero in equations (8)–(10) only if all atoms in the system are considered. In a finite system, the traces of $\hat{\rho}_e$, $\hat{\mu}_v$ and $\hat{\lambda}_v$ are thus conserved. This is not the case for an open system; while in a symmetric situation (identical environments on left and right of our device, no bias and static ions) the traces of $\hat{\mu}_v$ and $\hat{\lambda}_v$ may remain at zero because of exact cancellations, in general these traces will deviate from zero, and the trace of $\hat{\rho}_e$ (or the number of electrons in the system) will vary. However, as we have an open system, this is neither surprising nor incorrect.

2.2. Locality of operators

In a practical implementation of the scheme described above, we must truncate the environment treated explicitly at a finite size. The use of appropriate time evolution operators, coupled with the damping on the time evolution of the environment operator, gives a good approximation to a semi-infinite (or other) environment. We now consider the question of the locality of the electronic correlation operators.

It is well known [8, 9] that the electronic density matrix decays with distance (in 1D, the decay is exponential for insulators and follows a power law for metals). This shows that one of the implicit assumptions of this open boundary formalism (that of spatial locality of the operators) is a good one for the electronic density matrix. The other assumption of temporal locality is justified by the natural decay of the time operators with time, which is enhanced by the addition of the Γ_{E} damping term (which represents random dephasing events occurring in the body of the electrodes).

However, there are no results for locality of the electronic correlation matrices, $\hat{\mu}_v$ and $\hat{\lambda}_v$. Indeed, as will be shown in more detail elsewhere [10], these matrices do not in general decay spatially or temporally in small systems; for a large environment including scattering effects, locality both in time and space will naturally arise. The temporal decay in the environment is imposed in the same way as for the electronic density matrix, through the Γ_{E} damping term. Some other technique is needed to impose spatial localization of the device–environment terms $\hat{\mu}_{v\text{DE}}$ and $\hat{\lambda}_{v\text{DE}}$. Without this localization, the operators propagate down the lead and reflect off the (finite) ends, leading to highly undesirable results.

The simplest way to ensure spatial localization is to extend the damping used for the environment to the device–environment terms, so that equation (9) becomes

$$i\hbar \frac{\partial \hat{q}_{\text{DE}}}{\partial t} = \hat{H}_{\text{D}} \hat{q}_{\text{DE}} - \hat{q}_{\text{D}} \hat{H}_{\text{DE}} + \hat{H}_{\text{DE}} \hat{q}_{\text{E}} - \hat{q}_{\text{DE}} \hat{H}_{\text{E}} + i\hbar \hat{D}_{\text{DE}}^q - 2i\hbar \Gamma_{\text{DE}} (\hat{q}_{\text{DE}} - \hat{q}_{\text{ref}}). \tag{13}$$

The effect of this damping is primarily a temporal localization; however, as the initial values of $\hat{q}_{DE}$ are zero by definition a spatial localization also results (any propagation will travel at finite speed and so will have decayed away after a finite distance). Tests of the effects of this damping will be presented in section 3.1; empirically, we find that there is no need for $\Gamma_{DE} = \Gamma_E$. The physical mechanism represented by this damping requires further investigation, which will be given in a future work.

3. Practical implementation and tests

We now present practical tests of this formalism, working at the zeroth (Ehrenfest) and first moment levels. The model used was extremely simple: a chain of 1s atoms of mass 10 amu, with a hopping integral of -1 eV between nearest neighbours only, and an atomic spacing of 1.0 Å. A repulsive potential was fitted to give the correct equilibrium spacing, with a magnitude of 0.648 eV. The variation with distance was a simple power law, with an exponent of two for the hopping integral and four for the repulsive potential. The device consists of nine atoms, the central atom of which is given an on-site barrier of 1 eV, to act as a scattering centre. The leads are 16 atoms long, and the time integral for the environment covers the most recent 7.5 fs, with an environmental damping of $\Gamma_E = 0.1$ fs^{-1} for all quantities. The initial electronic density matrix (which is also the reference density matrix for the environment) is found by diagonalizing the Hamiltonian of a wire 1001 atoms long, and using the central 41×41 site portion of the resulting density matrix. A timestep of 0.008 fs was used throughout (after tests to establish the largest practical value).

We will present results for this system, starting with a consideration of the necessity for localization of $\hat{\mu}_{\nu DE}$ and $\hat{\lambda}_{\nu DE}$ and showing the effect of the chosen localization, and then moving on to the more interesting problem of current-induced heating.

3.1. Restricting ranges

We show the drain current into the central atom as a function of time in figure 1, for systems without and with the device–environment damping applied to $\hat{\lambda}_\nu$. The system is allowed to settle (with no applied bias) for 20 fs, at which point a bias of -1 V is applied linearly over 5 fs (this is achieved by shifting the onsite energy terms in the atoms in the left lead and the first four atoms in the device). At 35 fs, the central atom is given a classical kinetic energy (at which point the large oscillations in the current begin). Over the first 100 fs, the system is well behaved, yielding the expected behaviour (in line with Ehrenfest or zeroth moment simulations). However, without any damping on $\hat{\lambda}_{\nu DE}$ (top graph), exponentially growing ringing in the current (arising from ringing in $\hat{\lambda}_{\nu DE}$) leads to numerically unstable behaviour. With a small damping value ($\Gamma_{\lambda DE} = 0.05$ fs^{-1}, bottom graph), this behaviour is completely suppressed. The ringing does not depend on the timestep used or the details of the discretization of the time evolution operators; by following the evolution of $\hat{\lambda}$, it can be seen to arise from reflections from the ends of the leads. This clearly demonstrates the need for some form of damping to be applied; the technique described in section 2.2 has the advantage that it does not affect the trace of the operator and is computationally simple to implement and physically transparent.

To explore the effects of this device–environment damping term on the system, we consider the evolution of the system under Ehrenfest dynamics, with only the electronic density matrix used. figure 2 shows the current into the central atom at short times (figure 2(a)—the first 20 fs) and longer times (figure 2(b)—up to 250 fs). Apart from an expected decrease in the value of the current at early times due to suppression of the imaginary part of the density matrix, we
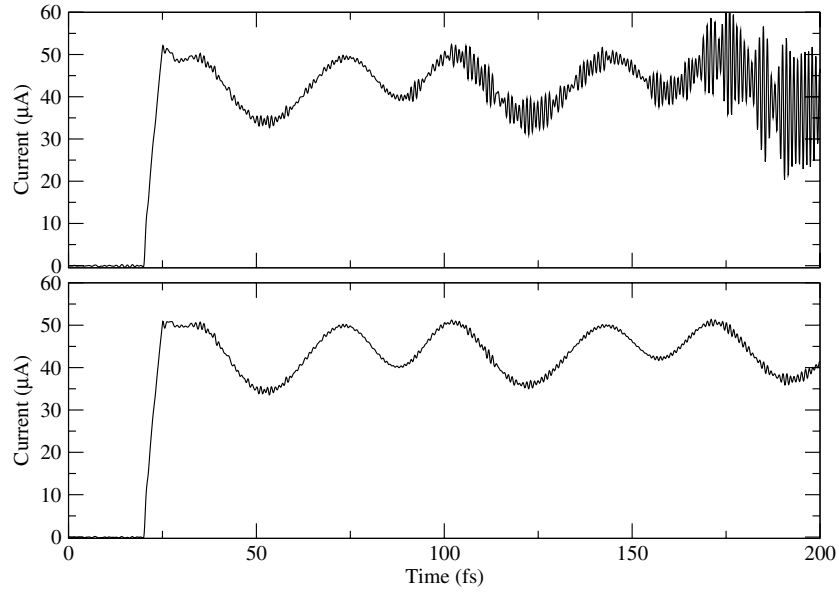
Figure 1. Current into central atom as a function of $\Gamma_{\lambda DE}$; $\Gamma_{\lambda DE} = 0.0$ (top) and $\Gamma_{\lambda DE} = 0.05$ (bottom). $\Gamma_{\lambda E}$ is 0.05 for both simulations. A bias of -1 V is applied at 20 fs and the ions are given classical kinetic energy at 35 fs (accounting for the oscillating current).

see two main effects: first, a reduction of noise and ringing, especially at long times; second, a subtle shift in the frequency of oscillation of the ion at long times. This arises from the change in the real part of the density matrix from the damping, which contributes to the ionic force, and places an upper limit on the acceptable size of the damping for the density matrix.

We will show below that there is a negligible effect on the heating calculated from the device–environment damping.

3.2. Current-induced heating

We show the current flowing into the central atom as a function of time, using the same parameters as in section 3.1, for Ehrenfest and first moment formalisms in figure 3. The damping applied to the density matrix was the same in both. As expected, we find that there is no difference between the two systems (any effect of the heating of the ions on the electrons, e.g. increased resistance, requires a second moment description of the ionic width and momentum). This reproduces our previous work in a closed system [4].

If we now turn to the heating, we recall that there are two components to the power at the first moment level: a term which integrates to give the classical kinetic energy ($\bar{P}_\nu^2/2M_\nu$) and another term arising from the electron–ion correlations producing a finite momentum spread for the ions, which we refer to as the quantum kinetic energy:

$$\bar{T}_Q = T_0 + \sum_\nu \int dt \, \frac{\text{Tr}\{\hat{F}_\nu \hat{\lambda}_\nu\}}{M_\nu}. \tag{14}$$

We consider first the quantum kinetic energy for a system *without* a barrier, which allows simple, direct comparison with the quantum perturbation result. Results for the quantum power ($\partial \bar{T}_Q/\partial t$) against bias (from 0.0 to 1.0 V) are shown in figure 4. The most striking point to note is that there are two regimes in the curve: a low bias regime, dominated by the zero-bias heating;
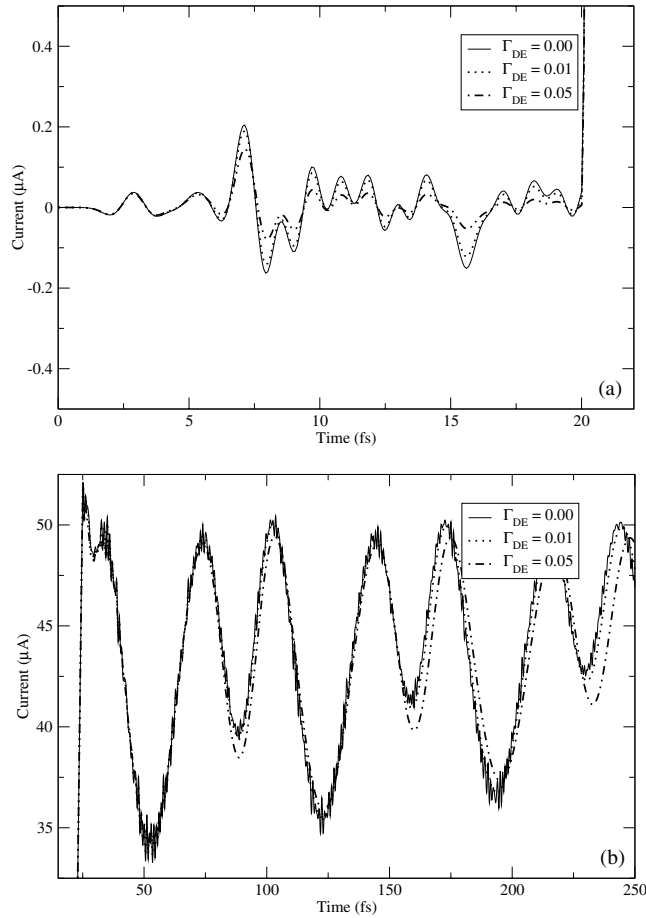
Figure 2. Current into central atom as a function of $\Gamma_{\rho DE}$. The simulation is Ehrenfest only. (a) Short times (0–25 fs). (b) Long times (20–200 fs). A bias of -1 V is applied at 20 fs and the ions are given classical kinetic energy at 35 fs (accounting for the oscillating current). The oscillations at short times arise from the starting state not being an exact eigenstate of the system.

and a higher bias regime, where the expected linear increase in power with bias is seen. The zero-bias heating arises because the initial states are not eigenstates of the correlated electron–ion system and there will be some non-zero coupling between ion and electrons. The rate of change of quantum power with bias in the linear region (fit between 0.5 and 1.0 V) is 0.292 μA, which is higher than the quantum perturbation result [3, 11] of 0.259 μA. This increase may result from the difference in regimes (the quantum perturbation result is for small biases), but arises primarily from the use of damping on the environment (Γ_E); we can test this effect by comparison with closed boundary solutions [4]. For short times (up to 5 fs), we achieve exact agreement with the closed boundary solutions, whose heating rates are in excellent agreement with the quantum perturbation result; for longer times, we find that increasing Γ_E increases the zero-bias heating rate, though there is a minimum value of Γ_E compatible with appropriate temporal localization of $\hat{\lambda}$. We show below that the localization of $\hat{\lambda}$ through Γ_{DE} only affects the quantum power weakly, as the force operator $\hat{F}_\nu$ is highly local (only nearest neighbour in this parametrization). We also find that the current entering the central atom increases linearly with bias and is in excellent agreement with the Landauer result. These results demonstrate
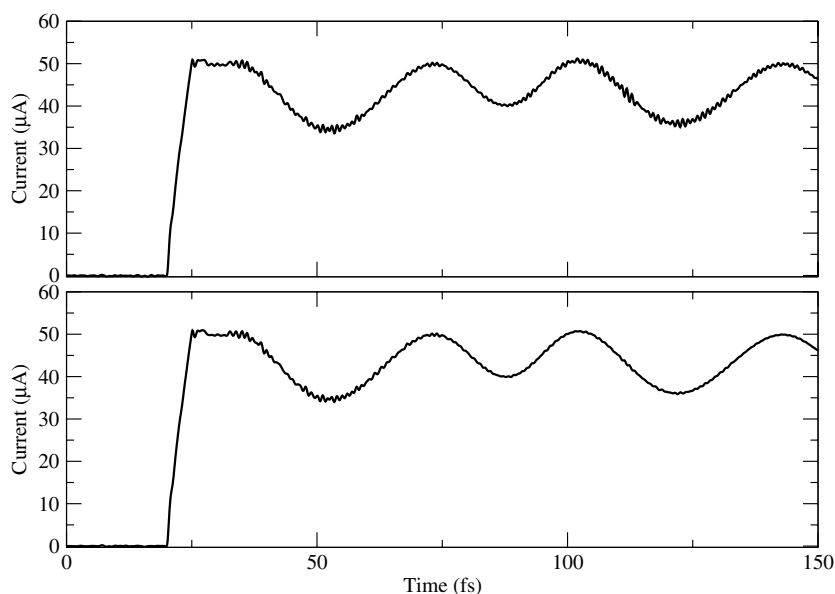
Figure 3. Current into central atom for a bias of −1 V with zeroth moment (bottom curve) and first moment (top curve) approximations.
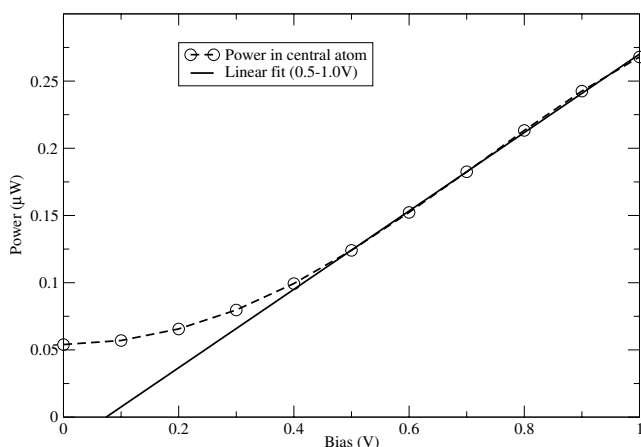

Figure 4. Quantum power as a function of bias for a simple, uniform linear chain. The solid line shows a linear fit to the data points between 0.5 and 1.0 V.

that, within reasonable limits, the approximations introduced by the open boundary formalism do not affect the results obtained. Having now established the reliability of the method, we consider further applications to the main system described above, with a central barrier.

The two contributions to the kinetic energy are plotted in figure 5 for biases between 0.0 and 1.0 V. As we have seen before, the quantum kinetic energy increases linearly with bias, and there is an accompanying increase in the frequency of oscillation of the ion. A slight wave is visible in the quantum kinetic energy which was not present in the closed system results. This is correlated with the oscillation of the ion and results from a large oscillation in Tr[$\hat{\lambda}$]. As mentioned above in section 2, the traces of the correlation matrices can be non-zero in the
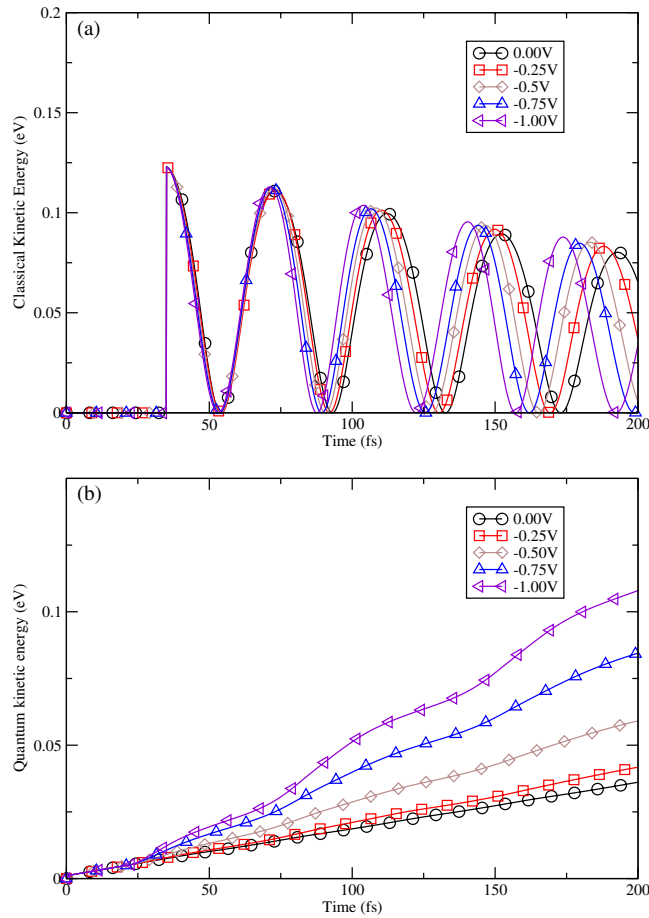
Figure 5. Classical (a) and quantum (b) contributions to the ionic kinetic energy as a function of time for biases between 0.0 and 1.0 V.

open boundary formalism. On application of a bias, the trace of $\hat{\lambda}$ shifts (but remains constant with a constant bias); once the ion is allowed to oscillate with some kinetic energy, the trace of $\hat{\lambda}$ also oscillates, with amplitude dependent on the applied bias. This leads to the ripples in the quantum kinetic energy.

We have tested that there are no effects coming from the device–environment damping which is applied to $\hat{\lambda}$ and $\hat{\mu}$ by varying the value of $\Gamma_{\lambda DE}$; these results are shown in figure 6 for values of $\Gamma_{\lambda DE}$ between 0.05 and 0.4. We have not shown results for varying $\Gamma_{\mu DE}$ as they overlie the curves for small $\Gamma_{\lambda DE}$. The effect on the quantum kinetic energy is almost too small to be distinguished, so we have also plotted the derivative $(\text{Tr}\{\hat{F}\hat{\lambda}\}/M)$. We see that the effect of $\Gamma_{\lambda DE}$ is negligible for small values.

3.3. Time propagation

While a closed form (which is truncated in time) has been found for the environment, we must propagate the device and device–environment terms numerically. We have chosen, as before [4, 5], to use the leapfrog method with a timestep of 0.008 fs. This is particularly helpful
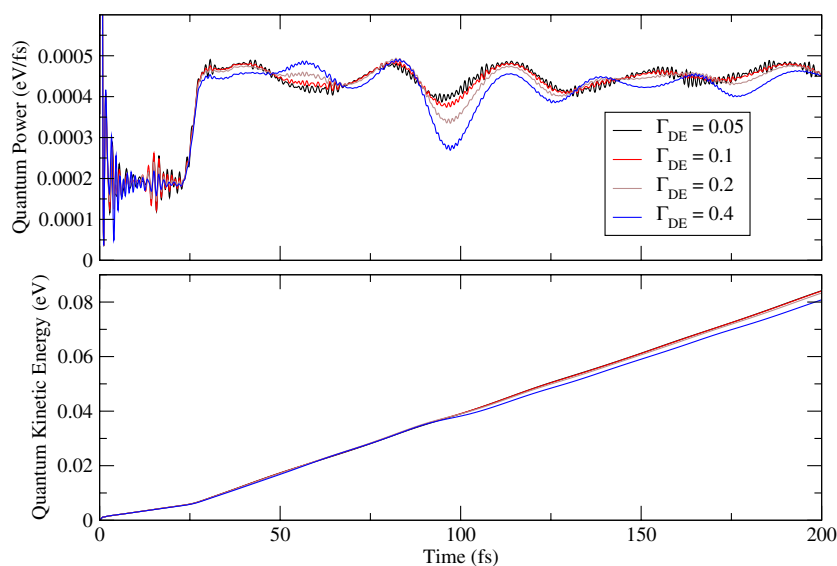
Figure 6. Effect of $\Gamma_{\lambda DE}$ on quantum heating of ions. Top: quantum power into the ion. Bottom: quantum kinetic energy. A bias of -0.5 V was applied after 20 fs over 5 fs, and the ion is given velocity at 35 fs.

with the open boundary formalism when compared to methods such as adaptive timestep techniques as it simplifies the interface between the numerical integral for the environment and the propagation for the device (in particular, the time evolution matrices can be calculated once at the start of the simulation for fixed timestep values and used without further processing). There is, however, a known drawback with this method when coupled equations or damped equations are used: a numerical instability can result with oscillation between even and odd timesteps, as can be seen in figure 7 (for a similar problem in a completely different field, see [12]). We find that one or two simple Euler steps ($f(t + \Delta t) = f(t) + \Delta t f'(t)$) every 500 or 1000 normal steps removes this instability, which results from the decoupling of odd and even timesteps and growth of parasitic (or unphysical) solutions [12]; this stability is shown in the lower curve of figure 7. A variety of more sophisticated schemes can be applied if further accuracy is needed.

4. Conclusions

We have described how to extend a general formalism for correlated electron–ion dynamics to open boundary conditions, and applied it specifically to the first moment expansion. We have shown that current-induced heating is correctly recovered at this level of approximation, and is in agreement with a quantum perturbative calculation within limits of the approximations required.

We have found that it is necessary to introduce damping on the electronic correlation matrices (for the fluctuation of the width of the ionic position and momentum). Without this damping, the simulation is unstable. However, the damping does not change the rate of heating calculated with the formalism.

As we have found before, the first moment approximation does not result in increased scattering of the electrons as the ionic kinetic energy increases. This requires second moments
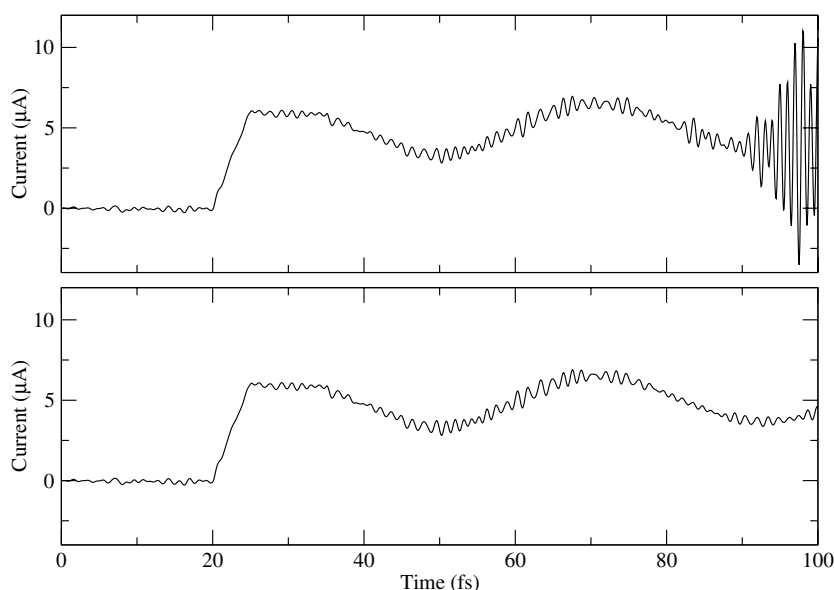
Figure 7. Current into device as a function of time; a bias of 0.1 V is applied at 20 fs over 5 fs. Top: pure leapfrog evolution. Bottom: leapfrog evolution with two Euler steps every 500 steps, which is equivalent to 4 fs.

(a theory which will be presented in future work), though we anticipate that the implementation within open boundaries should require only a trivial extension of the formalism in this paper.

Acknowledgments

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