9 SCIENTIFIC HIGHLIGHT OF THE MONTH

Correlated Electron-Ion Dynamics

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Abstract

Correlated Electron-Ion Dynamics (CEID) is an extension of molecular dynamics that allows us to introduce in a correct manner the exchange of energy between electrons and ions. The formalism is based on a systematic approximation (Small Amplitude Moment Expansion - SAME). This formalism is introduced, including modifications to account for open boundaries, its structure analysed, and some results given (the heating of an ion by current carrying electrons, and inelastic I-V spectroscopy). The computer code that implements the closed system version of the formalism (Dinamo) is described. We close with some thoughts about the future prospects of this approach.

1 Introduction

Molecular dynamics is a well-established computational method for studying the dynamical properties of materials[1]. The central idea is to allow a collection of atoms to move under the influence of forces according to Newton's second law of motion ($\ddot{R}_\nu = F_\nu/M_\nu$), where $R_\nu(t)$ is an atomic coordinate at time t, F_ν is the force on the coordinate and M_ν is an atomic mass. Different materials are accommodated through the choice of the expression for the force (which ranges from simple force fields[2] to high-level electronic structure calculations[3]) and the mass of the atoms. The immense utility of this approach stems from two things: its great generality and its obvious connection to the material world. The generality of force expression allows a huge array of materials to be considered (common examples include biological molecules[4] and metals subjected to high energy radiation[5]), while the generality of the dynamical equations allows a wide range of conditions to be considered (notably both equilibrium and non-equilibrium systems) through the choice of initial and boundary conditions[1, 6]. This is a remarkable achievement for one modelling technique.

Underlying conventional molecular dynamics is a pair of well-defined assumptions: the atoms can be treated as classical (that is, not-quantum) particles that follow precise trajectories; there exists a well-defined set of forces which are a function of atomic position (and possibly velocity). The latter assumption can be interpreted to mean that the electrons remain on one Born-Oppenheimer surface (in the absence of velocity dependent forces). This will be true provided the energy separation between the surfaces is greater than $\hbar\omega$, where ω is a characteristic atomic vibrational frequency. This clearly eliminates all metals. But even then the effects are small because the atomic forces from each of the Born-Oppenheimer surfaces sampled are rather similar to one another. The lowest order corrections can the approximately included by means of a velocity dependent force that introduces the loss of energy of fast atoms to the electrons[7], but this is negligible except for highly energetic atoms.

The above represents a state of affairs that applies to many materials problems. However, there are particular problems in which transitions between Born-Oppenheimer surfaces control the phenomena being investigated. Two problems of this type with which we are familiar are: irreversible exchange of energy between ions and current carrying electrons (leading to Joule heating and inelastic I-V spectroscopy); non-radiative relaxation of excited electrons (or polarons or electron-hole pairs) in polymers. Conventional molecular dynamics cannot handle these problems, so we need to introduce some modifications to accommodate them.

An approach used by a number of researchers when faced with these phenomena is the Ehrenfest approximation[8]. At the back of this is an exact set of results, namely the Ehrenfest *equations*[9] which are $\dot{\bar{R}}_\nu = \bar{P}_\nu/M_\nu$ and $\dot{\bar{P}}_\nu = \bar{F}_\nu$ where P_ν is a component of momentum. While these look like the ordinary equations of Newtonian mechanics, they of course involve quantum expectation values ($\bar{R}_\nu = \langle\Psi|\hat{R}|\Psi\rangle$, $\bar{P}_\nu = \langle\Psi|\hat{P}|\Psi\rangle$, $\bar{F}_\nu =$

$\langle\Psi| - \partial\hat{H}(\hat{R})/\partial\hat{R}_\nu|\Psi\rangle$ where $\hat{H}(\hat{R})$ and $|\Psi\rangle$ are the Hamiltonian and wavefunction for the whole system (electrons and ions)). The Ehrenfest *approximation* then makes an anzatz for $\bar{F}_\nu$ namely $\bar{F}_\nu = \langle\Phi| - \partial\hat{H}_e(\bar{R})/\partial\bar{R}_\nu|\Phi\rangle$. Thus the full Hamiltonian $\hat{H}(\hat{R})$ which depends on the ionic position *operator* $\hat{R}$ is replaced by the mean field Hamiltonian $\hat{H}(\bar{R}) = \hat{T}_I + \hat{H}_e(\bar{R})$ ($\hat{T}_I$ is the ionic kinetic energy operator) produced by substituting the ionic position operator by its expectation value, and the full wavefunction $|\Psi\rangle$ is replaced by the electronic wavefunction $|\Phi\rangle$ which obeys $\hat{H}_e(\bar{R})|\Phi\rangle = \mathrm{i}\hbar\partial|\Phi\rangle/\partial t$. This approximation describes some phenomena correctly (such as the excitation of electrons by fast ions), but others incorrectly (such as the heating of ions by current carrying electrons[10]).

The Ehrenfest approximation is attractive because it retains the good features of molecular dynamics (generality of systems and properties), while adding the new feature of being able to model some non-adiabatic processes. But it clearly needs further extensions to reproduce many other non-adiabatic processes, notably the excitation of ionic motion by energetic electrons.

In the next section we describe the basic mathematical structure of our method which allows us to model more general non-adiabatic processes[11], discuss a way of thinking about quantum mechanics that is particularly well suited to this problem, and then explain the behaviour of our method from this perspective. In the subsequent section this molecular dynamics approach is compared with established perturbative calculations[12, 13, 14]. We then look at an extension of the method to accomodate open boundaries[8], and describe the program used to implement the algorithm (DINAMO). Finally we report results obtained with our method, and then conclude with some thoughts about the future of this approach.

2 Moment expansion approach to CEID

2.1 Small Amplitude Moment Expansion (SAME)

2.1.1 Main equations

As we have described above, the Ehrenfest approximation is achieved by replacing the ionic position operator $\hat{R}_\nu$ by its expectation value $\bar{R}_\nu$. We now introduce fluctuations about this mean value through the quantity $\Delta\hat{R}_\nu = \hat{R}_\nu - \bar{R}_\nu$[11]. Instead of using wavefunctions it is much easier to work with the density matrix of the system $\hat{\rho}$, in terms of which we can immediately define an electronic density matrix $\hat{\rho}_e = \mathrm{Tr}_I\left\{\hat{\rho}\right\}$ where $\mathrm{Tr}_I\left\{\star\right\}$ means the trace over ionic coordinates. In a real space representation this would be $\hat{\rho}_e = \int \mathrm{d}\vec{R}\langle\vec{R}|\hat{\rho}|\vec{R}\rangle$. The equation of motion is the quantum Liouville equation

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}}{\partial t} = \left[\hat{H},\hat{\rho}\right] \tag{1}$$

where the square brackets signify a commutator: $\left[\hat{H},\hat{\rho}\right]=\hat{H}\hat{\rho}-\hat{\rho}\hat{H}$. This equation of motion is the foundation of our approach. If we write the Hamiltonian as $\hat{H}=\hat{T}_I+\hat{H}_e(\hat{R})$, then the Ehrenfest approximation can be written as

$$\dot{\bar{R}}_\nu=\frac{\bar{P}_\nu}{M_\nu},\qquad \dot{\bar{P}}_\nu=\bar{F}_\nu$$
$$\bar{F}_\nu=\mathrm{Tr}_e\left\{\hat{\rho}_e\left(-\frac{\partial\hat{H}_e(\bar{R})}{\partial\bar{R}_\nu}\right)\right\},\qquad \mathrm{i}\hbar\frac{\partial\hat{\rho}_e}{\partial t}=\left[\hat{H}_e(\bar{R}),\hat{\rho}_e\right]\tag{2}$$

where $\mathrm{Tr}_e\left\{\star\right\}$ means a trace over electronic degrees of freedom. Note that if we define the Ehrenfest energy by $E_{Ehrenfest}=\sum_\nu\bar{P}_\nu^2/2M_\nu+\mathrm{Tr}_e\left\{\hat{\rho}_e\hat{H}_e(\bar{R})\right\}$ the above equations of motion have the great virtue of conserving this energy.

Keeping the above in mind, we now derive a more general set of equations for which the Ehrenfest method is the lowest order approximation. The key physical idea is that atoms are well defined by classical trajectories ($\bar{R}_\nu$) but that these are slightly broadened (characterised by $\overline{\Delta R_\nu^2}$) because of the quantum nature of the ions. Thus we have:

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial\hat{\rho}_e}{\partial t} &= \mathrm{Tr}_I\left\{\left[\hat{T}_I+\hat{H}_e(\hat{R}),\hat{\rho}\right]\right\}\\
&= \mathrm{Tr}_I\left\{\left[\hat{H}_e(\bar{R})+\sum_\nu\Delta\hat{R}_\nu\frac{\partial\hat{H}_e(\bar{R})}{\partial\bar{R}_\nu}+\cdots,\hat{\rho}\right]\right\}\\
&= \left[\hat{H}_e(\bar{R}),\hat{\rho}_e\right]-\sum_\nu\left[\hat{F}_\nu,\hat{\mu}_{1,\nu}\right]+\ldots
\end{aligned}$$

where we have introduced the force operator $\hat{F}_\nu=-\partial\hat{H}_e(\bar{R})/\partial\bar{R}_\nu$, and the first moment $\hat{\mu}_{1,\nu}=\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\hat{\rho}\right\}$. In general the moments measure the ionic distribution[15, 16, 17] as a function of electronic state. We will provide a more intuitive explanation for this later on. Note that we will only keep terms in expansions that produce the effects we are interested in.

To evaluate the equation of motion for $\hat{\rho}_e$, we need to find $\hat{\mu}_{1,\nu}$. We do this by using its equation motion:

$$\begin{aligned}
\frac{\partial\hat{\mu}_{1,\nu}}{\partial t} &= \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\left[\hat{T}_I+\hat{H}_e(\hat{R}),\hat{\rho}\right]\right\}-\dot{\bar{R}}_\nu\hat{\rho}_e\\
&= \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\left[\hat{T}_I+\hat{H}_e(\bar{R})+\sum_{\nu'}\Delta\hat{R}_{\nu'}\frac{\partial\hat{H}_e(\bar{R})}{\partial\bar{R}_{\nu'}}+\cdots,\hat{\rho}\right]\right\}-\dot{\bar{R}}_\nu\hat{\rho}_e\\
&= \frac{\hat{\lambda}_{1,\nu}}{M_\nu}+\frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e(\bar{R}),\hat{\mu}_{1,\nu}\right]-\sum_{\nu'}\frac{1}{\mathrm{i}\hbar}\left[\hat{F}_{\nu'},\hat{\mu}_{2,\nu\nu'}\right]+\ldots
\end{aligned}$$

We have introduced two further moments: $\hat{\lambda}_{1,\nu}=\mathrm{Tr}_I\left\{\Delta\hat{P}_\nu\hat{\rho}\right\}$ and $\hat{\mu}_{2,\nu\nu'}=\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}\hat{\rho}\right\}$, where $\Delta\hat{P}_\nu=\hat{P}_\nu-\bar{P}_\nu$. We only need to keep electron-ion correlations in the first moments, but we need the width of the ions to appear somewhere, so we write

$$\hat{\mu}_{2,\nu\nu'}\approx C^{RR}_{\nu\nu'}\hat{\rho}_e$$

where $C^{RR}_{\nu\nu'} = \mathrm{Tr}\left\{\Delta\hat{R}_\nu \Delta\hat{R}_{\nu'}\hat{\rho}\right\}$. The equation of motion for $\hat{\lambda}_{1,\nu}$ is

$$\begin{aligned}\frac{\partial\hat{\lambda}_{1,\nu}}{\partial t} &= \frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e(\bar{R}), \hat{\lambda}_{1,\nu}\right] - \sum_{\nu'}\frac{1}{\mathrm{i}\hbar}\left[\hat{F}_{\nu'}, \hat{\chi}_{2,\nu\nu'}\right] + \\ & \frac{1}{2}\left(\Delta\hat{F}_\nu\hat{\rho}_e + \hat{\rho}_e\Delta\hat{F}_\nu\right) - \frac{1}{2}\sum_{\nu'}\left(\hat{K}_{2,\nu\nu'}\hat{\mu}_{1,\nu'} + \hat{\mu}_{1,\nu'}\hat{K}_{2,\nu\nu'}\right) + \ldots\end{aligned}$$

where $\hat{\chi}_{2,\nu\nu'} = \frac{1}{2}\mathrm{Tr}_I\left\{\left(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu\right)\hat{\rho}\right\} \approx C^{PR}_{\nu\nu'}\hat{\rho}_e$, and we have defined $C^{PR}_{\nu\nu'} = \frac{1}{2}\mathrm{Tr}\left\{\left(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu\right)\hat{\rho}\right\}$, $\hat{K}_{2,\nu\nu'} = \partial^2\hat{H}_e(\bar{R})/\partial\bar{R}_\nu\partial\bar{R}_{\nu'}$ (a sort of spring constant), $\Delta\hat{F}_\nu = \hat{F}_\nu - \bar{F}_\nu$, and $\bar{F}_\nu = \mathrm{Tr}_e\left\{\hat{\rho}_e\hat{F}_\nu\right\} - \sum_{\nu'}\mathrm{Tr}_e\left\{\hat{\mu}_{\nu'}\hat{K}_{\nu'\nu}\right\}$. To obtain closure we need equations of motion for $C^{RR}_{\nu\nu'}$ and $C^{PR}_{\nu\nu'}$. This involves introducing $C^{PP}_{\nu\nu'} = \mathrm{Tr}\left\{\Delta\hat{P}_\nu\Delta\hat{P}_{\nu'}\hat{\rho}\right\}$, and hence we have

$$\begin{aligned}\frac{\partial C^{RR}_{\nu\nu'}}{\partial t} &= \frac{C^{PR}_{\nu\nu'}}{M_\nu} + \frac{C^{PR}_{\nu'\nu}}{M_{\nu'}} \\ \frac{\partial C^{PR}_{\nu\nu'}}{\partial t} &= \frac{C^{PP}_{\nu\nu'}}{M_{\nu'}} + \mathrm{Tr}_e\left\{\hat{F}_\nu\hat{\mu}_{1,\nu'}\right\} - \sum_{\nu''}\bar{K}_{2,\nu\nu''}C^{RR}_{\nu''\nu'} \\ \frac{\partial C^{PP}_{\nu\nu'}}{\partial t} &= \mathrm{Tr}_e\left\{\hat{F}_\nu\hat{\lambda}_{1,\nu'} + \hat{\lambda}_{1,\nu}\hat{F}_{\nu'}\right\} - \sum_{\nu''}\left(C^{PR}_{\nu\nu''}\bar{K}_{2,\nu''\nu'} + \bar{K}_{2,\nu''\nu}C^{PR}_{\nu'\nu''}\right)\end{aligned}$$

where $\bar{K}_{2,\nu\nu'} = \mathrm{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\hat{\rho}_e\right\}$. We now have a closed set of equations. However, these involve many-electron density matrices which are computationally intractable. Thus we have to reduce the many-electron density matrices to single-electron matrices by tracing out all but one electron[11]. To produce closure we have to make a Hartree-Fock approximation for two-electron density matrices. But note that since the single particle density matrix is not in general idempotent we need to augment the usual result $\hat{\rho}^{(2)}_e(12, 1'2') = \hat{\rho}^{(1)}_e(1, 1')\hat{\rho}^{(1)}_e(2, 2') - \hat{\rho}^{(1)}_e(1, 2')\hat{\rho}^{(1)}_e(2, 1')$[18]. The formal procedure (taken only to first moment) is explained elsewhere[11], and the new result will be given in an upcoming paper. From now on, the equations will be for single-electron matrices.

2.1.2 A model of quantum mechanics

Having written down a set of opaque equations we need some way to understand them intuitively. This first requires us to have some way of thinking about quantum mechanical density matrices. In this context they are most naturally thought of as distribution functions corresponding to collections of trajectories (or Feynman paths: they do not need to correspond to solutions of an equation of motion). Thus the quantum width of an atom refers to the range of allowed trajectories available to it. Immediately we see that the average kinetic energy of an atom is not determined by the average momentum, but also by the spread of momentum

$$\bar{T}_I = \sum_\nu \frac{\overline{P^2_\nu}}{2M_\nu} = \sum_\nu \frac{1}{2M_\nu}\left(\bar{P}^2_\nu + \overline{\Delta P^2_\nu}\right)$$

Thus atomic heating (increase in kinetic energy) has two components: the “classical” component from the average momentum, and the “quantum” component from the spread in momentum.

The force from the atoms felt by the electrons depends on the positions of the atoms, and hence their trajectories. Thus a spread of atomic trajectories will produce a spread of forces on the electrons, and hence the spread of electronic trajectories. Likewise, a spread of electronic trajectories will produce a spread of forces on the atoms, and hence of atomic trajectories. We are now in a position to understand the SAME equations.

2.1.3 An interpretation of SAME

We begin with the simplest case, the Ehrenfest approximation. The atoms are clearly represented by just one trajectory ($\bar{R}_\nu(t)$), and so the quantum width is zero. This is reflected in the dynamics of the electrons which experience only $\hat{H}_e(\bar{R})$. Because there is no dispersion of atomic trajectories there is similarly no dispersion of the electronic trajectories.

This latter point can be seen most clearly by assuming that the electrons can be represented by a single Slater determinant. In this case the equation of motion for the electrons (in terms of the single particle density matrix) becomes

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t} = \left[\hat{H}_e^{(HF)}, \hat{\rho}_e^{(1)}\right]$$

where $\hat{H}_e^{(HF)}$ is the Fock matrix. If $\hat{H}_e^{(HF)}|\psi_n^{(1)}(t)\rangle = \mathrm{i}\hbar\frac{\partial}{\partial t}|\psi_n^{(1)}(t)\rangle$ where $|\psi_n^{(1)}(t)\rangle$ is a single-particle state, and $\hat{\rho}_e^{(1)} = \sum_n |\psi_n^{(1)}(t)\rangle f_n \langle\psi_n^{(1)}(t)|$, then we find that $\partial f_n/\partial t = 0$. Thus the eigenspectrum of the density matrix remains unchanged, and if the electronic system starts as a single Slater determinant, it remains so for evermore. This is what we mean by a single electron trajectory. Thus the Ehrenfest approximation corresponds to representing the electrons and ions individually as single trajectories that interact with one another.

Another way of phrasing this is that the Ehrenfest approximation is a mean field approximation in which all fluctuations have been suppressed. It is this feature that prevents it from properly describing the flow of energy from electrons to the ions[10]: the ions see the electrons as a cold gas regardless of the state of excitation (defined by the occupancies f_n), and so heat flows predominantly from ions to electrons. There can be a small flow the other way if the mean electron density becomes sufficiently rough, but this still provides quantitatively wrong results[8].

Thus we see that the correct energy transfer requires the electron gas to have its fluctuations restored, which by our earlier arguments means that the ions must also be allowed to fluctuate about their mean trajectory. Quantitative results can be obtained at the level of the first moment (see later in this article for results). The explanation is as follows.

Consider first the equation motion for the electrons

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t}=\left[\hat{H}_e^{(HF)},\hat{\rho}_e^{(1)}\right]-\sum_\nu \mathrm{Tr}_I\left\{\left[\Delta\hat{R}_\nu\hat{F}_\nu^{(1)},\hat{\rho}^{(1)}\right]\right\}$$

where we have unpacked $\hat{\mu}_{1,\nu}^{(1)}$. The first term is just the Ehrenfest term, so we focus on the second one. The quantity $\Delta\hat{R}_\nu\hat{F}_\nu^{(1)}$ gives the linear variation of the force felt by the electrons due to the ions with displacement of the ionic trajectory from the mean trajectory. Thus, dispersion in the ionic trajectory will now produce dispersion in the electronic trajectories.

To see explicitly what is meant by dispersion of electron trajectories let us write $\mathrm{i}\hbar\hat{\Gamma}^{(1)}=-\sum_\nu\left[\hat{F}_\nu^{(1)},\hat{\mu}_{1,\nu}^{(1)}\right]$ so that

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t}=\left[\hat{H}_e^{(HF)},\hat{\rho}_e^{(1)}\right]+\mathrm{i}\hbar\hat{\Gamma}^{(1)}\tag{3}$$

As above, we now write $\hat{\rho}_e^{(1)}=\sum_n|\psi_n^{(1)}(t)\rangle f_n\langle\psi_n^{(1)}(t)|$, which after inserting into equation (3) gives

$$\frac{\partial f_n}{\partial t}=\langle\psi_n^{(1)}(t)|\hat{\Gamma}^{(1)}|\psi_n^{(1)}(t)\rangle$$

Thus the occupancies can now change. This means that if we started from a single Slater determinant, this must evolve into an incoherent sum of determinants corresponding to evolving fluctuations in the electron gas. That is, we now must write:

$$\hat{\rho}_e^{(1)}=\sum_m\wp_m\hat{\rho}_{e,m}^{(1)}$$

where $\hat{\rho}_{e,m}^{(1)}$ is produced from a single Slater determinant and evolves as $\mathrm{i}\hbar\partial\hat{\rho}_{e,m}^{(1)}/\partial t=\left[\hat{H}_e^{(HF)},\hat{\rho}_{e,m}^{(1)}\right]$ and $\wp_m$ is the probability of being in that state, and itself evolves in response to ionic fluctuations.

So far we have not considered the explicit width of the ionic bundle of trajectories. This information is present in $\hat{\mu}_{1,\nu}^{(1)}$, but has to get there from somewhere, and that somewhere is the equation of motion which we can write as

$$\frac{\partial\hat{\mu}_{1,\nu}^{(1)}}{\partial t}=\frac{\hat{\lambda}_{1,\nu}^{(1)}}{M_\nu}+\frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e^{(HF)},\hat{\mu}_{1,\nu}^{(1)}\right]-\frac{1}{\mathrm{i}\hbar}\sum_{\nu'}C_{\nu\nu'}^{RR}\left[\hat{F}_{\nu'}^{(1)},\hat{\rho}_e^{(1)}\right]$$

Information about the ionic width is provided explicitly by $C_{\nu\nu'}^{RR}$. It also propagates through from $\hat{\lambda}_{1,\nu}^{(1)}$ which depends on $C_{\nu\nu'}^{PR}$.

Thus, by keeping electron-ion correlations up to the first moment ($\hat{\mu}_{1,\nu}^{(1)}$ and $\hat{\lambda}_{1,\nu}^{(1)}$) and using the mean field expressions for the second moments ($\hat{\mu}_{2,\nu\nu'}\approx C_{\nu\nu'}^{RR}\hat{\rho}_e$ *etc.*) we are able to capture many important features (see below for results) deriving from the interaction of time-evolving fluctuating electrons and ions.

2.2 Analytical features of the method

We will now discuss several analytical properties of the method. We have continually found these properties helpful both as a reality check and, in a broader sense, as an additional source of insight into CEID and into the dynamical processes that the SAME algebra represents.

2.2.1 Detailed balance and statistical properties

Let us return to the question of electronic transitions driven by the electron-ion correlations, viewed this time at the many-electron level. Let $|\alpha\rangle = |\alpha(t)\rangle$ and $P_\alpha = P_\alpha(t)$ be the eigenvectors and eigenvalues of the many-electron density matrix $\hat{\rho}_e$ so that

$$\hat{\rho}_e = \sum_\alpha |\alpha\rangle \, P_\alpha \, \langle\alpha|$$

Then SAME enables us to write the equation of motion for $\hat{\rho}_e$ in the form

$$\mathrm{i}\hbar\dot{\hat{\rho}}_e = [\hat{H}_e, \hat{\rho}_e] + \hat{\Sigma}\hat{\rho}_e - \hat{\rho}_e\hat{\Sigma}^\dagger + G[\hat{\rho}_e] \tag{4}$$

and to obtain explicit forms for the self-energy-like operator $\hat{\Sigma}$ and for the superoperator $G[\hat{\rho}_e]$, which remain valid for restricted, but finite, lengths of time after the combined electron-ion system has been allowed to evolve. Leaving these forms to a future paper, let us here concentrate on the following results.

The hermitian part of $\hat{\Sigma}$ constitutes an effective correction to $\hat{H}_e$. The resultant new effective Hamiltonian for the electrons would, by itself, produce unitary temporal evolution with constant P_α. As was indicated earlier, this is the type of evolution that would be obeyed by an isolated system of electrons, or by electrons that interact with their surroundings through at most mean field interactions.

The antihermitian part of $\hat{\Sigma}$, together with $G[\hat{\rho}_e]$, on the other hand, drives transitions in the density matrix, which manifest themselves as time-variation in its eigenvalues. This means that even if the combined electron-ion system is described by a pure state (a single state-vector that could itself of course be a coherent superposition of other state-vectors), the electron subsystem itself cannot be described in that way. Instead, after tracing out the ionic degrees of freedom, we are left with an effective description of the electrons given by an incoherent mix of many-electron state-vectors (the eigenvectors of $\hat{\rho}_e$), with time-dependent weights. The propagation of this incoherent mix of states furthermore cannot be described by a single effective hermitian electronic Hamiltonian, for if it could, then an initially pure electronic state would not split into an incoherent shower in the first place.

Notionally, we could think of this incoherent shower of electronic states as a collection of independent quantum electronic evolutions, corresponding to different possible evolutions of the original correlated electron-ion system. It is a strength of SAME, however, that we do not have to make this interpretation. We do not, furthermore, have to in any way prejudge the nature of the evolution of the shower. We do not, in particular, have to attempt to impose *ad hoc* forms on the above transitions, such as hops – instantaneous or not, random or not – between different states. These processes are allowed to take place naturally, in whatever way the quantum Liouville equation dictates. Indeed, SAME is as accurate – within a given level of the moment expansion – as the many-body electron-ion time-dependent Schrödinger equation (TDSE). A strength of SAME though is that by breaking down the TDSE into interpretable terms, it helps us understand the processes described by this equation.

The forms of $\hat{\Sigma}$ and $G[\hat{\rho}_e]$, furthermore, are such that the time-varying eigenvalues of $\hat{\rho}_e$ obey a rate equation of the form

$$\dot{P}_\alpha = \sum_\beta \left(-P_\alpha \, W_{\alpha\beta} + P_\beta \, W_{\beta\alpha} \right) \tag{5}$$

where the coefficients $W_{\alpha\beta}$ are set by $\hat{\Sigma}$. Since $\hat{\Sigma}$ depends on $\hat{\mu}_1$ and since the propagation of the latter is driven by $\hat{\rho}_e$, the coefficients $W_{\alpha\beta}$ can themselves be viewed as functions of the density matrix. Equation (5) therefore relates the rate of change of every P_α to the microscopic content of $\hat{\rho}_e$, and for this reason, at least for the purposes of the present discussion, we regard equation (5) as a statement of detailed balance. Equation (5) comes about as a consequence of SAME. It is not an *a priori* stipulation.

Let us now briefly turn to another question. Let us go back to the world of classical mechanics and ask, how would one go about writing down an analogue of SAME for a system of classical interacting electrons and ions. The first question we would have to resolve is what quantity, if any, is to take up the role of moment operators such as $\hat{\mu}_{1,\nu}$. There is but one possible answer. We would first and foremost have to consider a statistical ensemble of copies of our correlated electron-ion system, described by a classical phase-space distribution function $f(\vec{r}, \vec{p}, \vec{R}, \vec{P}, t)$, where lower- and upper-case symbols represent classical electron and ion canonical variables respectively. *Then* we can define the classical analogue of $\hat{\mu}_{1,\nu}$ (now a scalar function of $\vec{r}, \vec{p}$)

$$\mu_{1,\nu} = \int \Delta R_\nu \, f(\vec{r}, \vec{p}, \vec{R}, \vec{P}, t) \, \mathrm{d}\vec{R} \mathrm{d}\vec{P}$$

where $\Delta R_\nu = R_\nu - \bar{R}_\nu$, $\bar{R}_\nu = \int R_\nu \, f(\vec{r}, \vec{p}, \vec{R}, \vec{P}, t) \, \mathrm{d}\vec{r} \mathrm{d}\vec{p} \mathrm{d}\vec{R} \mathrm{d}\vec{P}$. For the actual development of the classical moment expansion (based on the classical Liouville equation), we would expect an algebraically analogous route to above, with certain replacements: electronic operators become scalar functions in the classical phase space; traces become phase-space integrals; $[\, , \,]/\mathrm{i}\hbar$ turns into a corresponding Poisson bracket.

While this mapping from quantum to classical SAME may seem trivial, it has the following implication. Suppose that quantum mechanics, and, in particular, the quantum state-vector $|\Psi\rangle$ (e.g. that for the combined electron-ion system, but also more generally) and the TDSE, described a single system (as opposed to an ensemble). Then, since as we have seen the TDSE leads to SAME in the quantum case, we would expect Hamilton's equations of motion to lead to a classical form of SAME for the corresponding classical system.

But we have just argued that we may write down a classical form of SAME only for a classical ensemble, not for a single system. Therefore, we have to conclude that quantum mechanics, and $|\Psi\rangle$ and the TDSE in particular, describe an appropriate (quantum) ensemble of copies of a given system, and not a single system. Of course, this statistical view of quantum mechanics is known. But we have found that the SAME description of interacting many-particle systems makes it especially compelling and intuitive (and the other way round).

2.2.2 Connection with electron-phonon perturbation theory

A widely used tool in the theory of electron-phonon interactions is a model electron-phonon Hamiltonian, based on an expansion of the true electron-ion Hamiltonian to second order in the ionic displacements on some reference Born-Oppenheimer surface. We could make this expansion in two ways. If we expand about the equilibrium classical ionic positions, R_0, on that surface, then we obtain the Hamiltonian [10]

$$\hat{H}_0 = \hat{H}_e(R_0) - \sum_\nu \hat{F}_\nu(R_0)\hat{X}_\nu + \hat{T}_I + \frac{1}{2}\sum_{\nu,\nu'} \hat{X}_\nu K_{\nu\nu'}\hat{X}_{\nu'} \tag{6}$$

where $\hat{X}_\nu = \hat{R}_\nu - (R_0)_\nu$ and K is the Born-Oppenheimer dynamical response matrix. The first term describes unperturbed electrons, in a phonon-free environment, with relaxed frozen classical ions. The second term is the electron-phonon interaction. The last two terms describe unperturbed Born-Oppenheimer phonons. This is the standard electron-phonon Hamiltonian in solid state theory.

Making the expansion about $\bar{R}$ instead, in the spirit of SAME, yields the closely related Hamiltonian [10]

$$\bar{H} = \hat{H}_e(\bar{R}) - \sum_\nu \hat{F}_\nu(\bar{R})\Delta\hat{R}_\nu + \hat{T}_I + \frac{1}{2}\sum_{\nu,\nu'} \Delta\hat{R}_\nu K_{\nu\nu'}\Delta\hat{R}_{\nu'} \tag{7}$$

For small variations in $\bar{R}$ about R_0, the two Hamitonians are equivalent.

Our task now is to show that SAME, applied to $\bar{H}$, yields the same lowest-order electron-phonon transition rates, as standard electron-phonon perturbation theory, applied to $\hat{H}_0$. The purpose of the exercise is to demonstrate that despite its different algebraic appearance, SAME incorporates the selection rules that control inelastic transitions.

For simplicity, we consider non-interacting electrons and just one dynamical ionic degree of freedom, so that the index ν can be dispensed with. All electronic operators below are one-electron operators and we dispense with superscript 1 for simplicity. We ignore variations in $\bar{R}$, with $\bar{R} \approx R_0$, so that the two Hamiltonians above are now the same and we can dispense with the arguments of $\hat{H}_e$ and $\hat{F}$. Consider first the equations of motion for the ionic moments. They now read

$$\dot{C}^{RR} = \frac{2}{M}C^{PR}$$

$$
\begin{aligned}
\dot{C}^{PR} &= \frac{C^{PP}}{M} - KC^{RR} + \mathrm{Tr}_e \left\{ \hat{F}\hat{\mu} \right\} \\
\dot{C}^{PP} &= -2KC^{PR} + 2\mathrm{Tr}_e \left\{ \hat{F}\hat{\lambda} \right\} \qquad (8)
\end{aligned}
$$

where, for short, we have written $\hat{\mu}$ ($\hat{\lambda}$) for $\hat{\mu}_1$ ($\hat{\lambda}_1$). The physics described by these equations is the following. The quantity

$$
w = \frac{1}{M} \mathrm{Tr}_e \left\{ \hat{F}\hat{\lambda} \right\} \qquad (9)
$$

is the power dissipated into the ion by the electrons [10]. This power comes in as kinetic energy. It is then repartitioned, between kinetic and potential energy, via the quantity C^{PR}, which effectively mediates the communication between the two ionic canonical variables (momentum and position). This conduction of heat around ionic phase space, however, is modulated by the electrons, via the last term in the second one of equations (8). Indeed, we know that lattice heat conduction in metals is heavily suppressed by phonon-electron scattering.

Let us now turn to the equations of motion for the electronic density matrix and moment operators. Making use of the Hartree-Fock relation for the two-electron density matrix, given earlier, we obtain

$$
\dot{\hat{\rho}}_e = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\rho}_e] - \frac{1}{\mathrm{i}\hbar} [\hat{F}, \hat{\mu}] \qquad (10)
$$

$$
\dot{\hat{\mu}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\mu}] - \frac{1}{\mathrm{i}\hbar} C^{RR} [\hat{F}, \hat{\rho}_e] + \frac{\hat{\lambda}}{M} \qquad (11)
$$

$$
\dot{\hat{\lambda}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\lambda}] + \frac{1}{2} (\hat{F}\hat{\rho}_e + \hat{\rho}_e\hat{F}) - \hat{\rho}_e\hat{F}\hat{\rho}_e - \frac{1}{\mathrm{i}\hbar} C^{PR} [\hat{F}, \hat{\rho}_e] - K\hat{\mu} \qquad (12)
$$

We imagine releasing the electron-ion system from an initial product state, in which $\hat{\rho}_e$ commutes with $\hat{H}_e$, while the vibrations are in a harmonic-oscillator eigenstate with N phonons and with $C^{PR} = 0$. In the absence of electron-phonon interactions, the two subsystems would remain in that state forever.

The electron-phonon interaction is realised by the quantity $\hat{F}$. To do a lowest-order perturbative calculation we therefore now have to linearise the above equations in $\hat{F}$. Thus, we set $C^{PR} = 0$, $C^{RR} = C^{RR}(0) = n\hbar\omega/K$, $n = N + 1/2$, $\omega^2 = K/M$, and drop the last term in equation (10). This leaves us with two coupled equations for $\hat{\mu}$ and $\hat{\lambda}$. Taking matrix elements of these two equations in two eigenstates of $\hat{\rho}_e$ (and of $\hat{H}_e$), with occupations f_α, f_β and energies E_α, E_β, and defining $\hat{z} = K\hat{\mu}$ we get

$$
\begin{aligned}
\dot{z}_{\alpha\beta} &= -\mathrm{i}\omega_{\alpha\beta} z_{\alpha\beta} + \omega^2 \lambda_{\alpha\beta} + \mathrm{i}n\omega(f_\beta - f_\alpha)F_{\alpha\beta} \\
\dot{\lambda}_{\alpha\beta} &= -\mathrm{i}\omega_{\alpha\beta}\lambda_{\alpha\beta} - z_{\alpha\beta} + \left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta \right) F_{\alpha\beta}
\end{aligned}
$$

where $\hbar\omega_{\alpha\beta} = E_\alpha - E_\beta$. The solution for $\lambda_{\alpha\beta}$ is

$$
\lambda_{\alpha\beta} = \frac{1}{2} \frac{F_{\alpha\beta}}{\omega^2 - \omega_{\alpha\beta}^2} \{ \exp[\mathrm{i}(\omega_{\beta\alpha} + \omega)t] \, (P/\mathrm{i}\omega - Q) - \exp[\mathrm{i}(\omega_{\beta\alpha} - \omega)t] \, (P/\mathrm{i}\omega + Q) + 2Q \}
$$

where

$$P = -n\omega\omega_{\alpha\beta}(f_\beta - f_\alpha) + \omega^2\left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta\right)$$
$$Q = -\mathrm{i}n\omega(f_\beta - f_\alpha) + \mathrm{i}\omega_{\alpha\beta}\left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta\right)$$

Substituting this into equation (9) and taking the long-time limit (when $(\sin\omega t)/\omega \to \pi\delta(\omega)$), gives (with a factor of 2 added for spin degeneracy)

$$\begin{aligned} w &= \frac{\pi}{M}\sum_{\alpha,\beta}|F_{\alpha\beta}|^2\{\delta(\omega_{\beta\alpha}+\omega)[-(N+1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta] \\ &+\delta(\omega_{\beta\alpha}-\omega)[(N+1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta]\} \end{aligned}$$

This expression is algebraically identical (after some rearrangement) to the corresponding result for the power dissipated into phonons by excited electrons obtained by first-order scattering theory based on the standard electron-phonon Hamiltonian $\hat{H}_0$ given earlier [13].

We have demonstrated in a previous paper [11] that SAME, already at the level of the first moment, indeed reproduces the above analytical result in actual numerical simulations of ionic heating in a current carrying atomic wire. This agreement is highly significant because, unlike the argument above, the SAME equations on which the simulations are based do not make use of any reference Born-Oppenheimer surfaces, nor are these simulations perturbative.

Let us now consider the transition rates directly in $\hat{\rho}_e$. The solution for $z_{\alpha\beta} = K\mu_{\alpha\beta}$ is

$$z_{\alpha\beta} = \frac{1}{2}\frac{F_{\alpha\beta}}{\omega^2 - \omega_{\alpha\beta}^2}\{\exp[\mathrm{i}(\omega_{\beta\alpha}+\omega)t]\,(-P + \mathrm{i}\omega Q) - \exp[\mathrm{i}(\omega_{\beta\alpha}-\omega)t]\,(P + \mathrm{i}\omega Q) + 2P\}$$

From equation (10) we have

$$\dot{\rho}_{\alpha\alpha} = \frac{2}{\hbar}\,\mathrm{Im}\sum_\beta F_{\beta\alpha}\mu_{\alpha\beta}$$

Substituting in and taking the long-time limit gives

$$\begin{aligned} \dot{\rho}_{\alpha\alpha} &= \frac{2\pi}{\hbar}\frac{\hbar}{2M\omega}\sum_\beta |F_{\alpha\beta}|^2\{\delta(E_{\beta\alpha}+\hbar\omega)[(N+1/2)(f_\beta - f_\alpha) - (f_\beta + f_\alpha)/2 + f_\alpha f_\beta] \\ &+\delta(E_{\beta\alpha}-\hbar\omega)[(N+1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta]\} \end{aligned}$$

This is algebraically identical to

$$\begin{aligned} \dot{\rho}_{\alpha\alpha} &= \frac{2\pi}{\hbar}\frac{\hbar}{2M\omega}\sum_\beta |F_{\alpha\beta}|^2\{-(N+1)f_\alpha(1-f_\beta)\delta(E_{\beta\alpha}+\hbar\omega) - Nf_\alpha(1-f_\beta)\delta(E_{\beta\alpha}-\hbar\omega) \\ &+(N+1)f_\beta(1-f_\alpha)\delta(E_{\beta\alpha}-\hbar\omega) + Nf_\beta(1-f_\alpha)\delta(E_{\beta\alpha}+\hbar\omega)\} \end{aligned}$$

The latter is the known quantum correlated electron-phonon scattering-rate expression, which incorporates the selection rules for inelastic current-voltage spectroscopy [14]. Therefore, we expect SAME, at the level of the second moment, to capture inelastic transport spectral features. We will demonstrate by direct numerical simulations later on that this is indeed the case. The above analytical results incorporate also the ingredients needed for making the crossover from ionic heating, via thermal equilibrium, to ionic cooling, in the presence of an excited electron gas, as a function of the effective phonon energy [12]. We therefore assert that SAME enables us to monitor directly the flow of heat back and forth between the two subsystems, with the added advantages that SAME is not a perturbative scheme, that it makes no use of any Born-Oppenheimer reference surfaces, that it implicitly accounts for anharmonicity and that it is, above all, a form of MD that portrays these processes in real time.

2.3 Infinite lead current formalism

One area where the interaction between electrons and ions (and the transfer of energy between the different subsystems) is important is in the area of conduction of nanostructures, e.g. atomic-scale wires[19]. To examine problems of this nature, we need to be able to consider a device (where the physics which we are concerned with is localised) connected to an environment, which might typically be a pair of leads (allowing exchange of electrons and energy with the surroundings). In the description below we explicitly consider two leads, working at the Ehrenfest level, though the formalism extends in principle to a much broader environment model, and to the higher moment expansions (details will be presented in a paper under preparation).

We start from the quantum Liouville equation, Eq. (1), and divide the system into two regions: a device, labelled D, and the environment, labelled E. Then we can write:

$$\begin{aligned} \mathrm{i}\hbar\frac{\partial\hat{\rho}_D}{\partial t} &= [\hat{H}_D,\hat{\rho}_D] + (\hat{H}_{DE}\hat{\rho}_{ED} - \hat{\rho}_{DE}\hat{H}_{ED}) && (13)\\ \mathrm{i}\hbar\frac{\partial\hat{\rho}_{DE}}{\partial t} &= \hat{H}_D\hat{\rho}_{DE} - \hat{\rho}_D\hat{H}_{DE} + \hat{H}_{DE}\hat{\rho}_E - \hat{\rho}_{DE}\hat{H}_E && (14)\\ \mathrm{i}\hbar\frac{\partial\hat{\rho}_E}{\partial t} &= [\hat{H}_E,\hat{\rho}_E] + (\hat{H}_{ED}\hat{\rho}_{DE} - \hat{\rho}_{ED}\hat{H}_{DE}) \\ &- 2\mathrm{i}\hbar\Gamma_E(\hat{\rho}_E - \hat{\rho}_{ref}), && (15)\end{aligned}$$

where a damping term, $2\mathrm{i}\hbar\Gamma_E(\hat{\rho}_E - \hat{\rho}_{ref})$, has been introduced to the environment and will be descibed below.

Now we can apply different time evolution schemes to the environment (which we want to act as a bath of energy and electrons) and the device. For the environment, we seek a closed, integral form. We assume that the Hamiltonian is static. If we define a driving term $\mathrm{i}\hbar\hat{G}_E = (\hat{H}_{ED}\hat{\rho}_{DE} - \hat{\rho}_{ED}\hat{H}_{DE})$ and define the value of the reference driving term by $0 = [\hat{H}_E,\hat{\rho}_E(0)] + \mathrm{i}\hbar\hat{G}_E^{(0)} - 2\mathrm{i}\hbar\Gamma(\hat{\rho}_E(0) - \hat{\rho}_{ref})$, then we can write:

$$\hat{\rho}_E(t) = \hat{\rho}_E(0) + \int_0^t \mathrm{d}x\ \hat{O}(x)\left(\hat{G}_E(t-x) - \hat{G}_E^{(0)}\right)\hat{O}^\dagger(x), \qquad (16)$$

where $\hat{O}(t) = \mathrm{e}^{-\Gamma_E t}\mathrm{e}^{\hat{H}_E t/\mathrm{i}\hbar}$ is a time evolution operator which arises from the commutator of $\hat{\rho}_E$ and $\hat{H}_E$, and includes the damping introduced in Eq. (15). The effect of this scattering-like Γ_E term will be to localise $\hat{\rho}_E(t)$ in time, enhancing the natural time localisation of the time evolution operators[8].

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

$$\hat{O}(t) = e^{-\Gamma_E t} \int \mathrm{d}E e^{Et/\mathrm{i}\hbar} \lim_{\eta \to 0^+} \mathrm{Im} \left(-\frac{1}{\pi} \right) \hat{g}(E + \mathrm{i}\eta). \tag{17}$$

These operators implicitly include the semi-infinite environment given by the Green's functions; when coupled with the reference density matrix, $\hat{\rho}_{ref}$, for a similar environment they give a restoring force towards the chosen semi-infinite system whatever the size of the explicit environment chosen.

For the device and device-environment terms, we use the leapfrog method to evolve the equations forward in time; this is also used by the DINAMO code.

2.4 Implementation of DINAMO

The computational implementation of the SAME has been named DINAMO, which stands for Dynamics in Non-Adiabatic Molecular Orbitals. This is a code written from scratch in Fortran 90, which at present roughly consists of 10k lines of code, and is an implementation of the SAME equations for orthogonal tight binding Hamiltonians. The following methodologies have been implemented:

- Geometry optimization, using an efficient quasi-Newton algorithm [20, 21].
- Born-Oppenheimer molecular dynamics.
- Ehrenfest dynamics.
- First moment SAME.
- Second moment SAME.

Self consistency is implemented at the BO and Ehrenfest levels via point charge inter-site Coulomb interactions and an onsite Hubbard "U" like term[22].

All input is handled using the FDF package written by Alberto Garcia and Jose Soler (used in the SIESTA code) which makes input files easy to read and edit and provides great flexibility. All parameters are read from a single input file (which may be separated in different files using FDF's "include" capabilities). Most input parameters will acquire sensible default values when not explicitly defined.

In a tight binding basis set, all SAME equations of motion are equations between matrices. Operations like commutators and matrix products are required to calculate the derivatives of the different operators in their equations of motion and they represent the bottleneck of the calculation. These operations must be optimized to achieve maximum performance. At the core of the code is a purpose built linear algebra module which implements all matrix operations, including additions and multiplications by scalars. Although some of these operations could be dealt with by using Fortran 90 array features, we have chosen to encapsulate them in the linear algebra module. In this way, parallelization, vectorization or changes in the storage structures can be restricted to the internal workings of the module and no modification of the rest of the code is needed. A new Fortran type `matrix` is defined, the structure of which is hidden from the user. Using the abstract matrix operations, the implementation of the SAME equations is a matter of translating the algebra into these operations. This made the task of implementing and debugging the SAME equations relatively straightforward since never in the code is an actual element of any of the operators explicitly modified or referenced.

The Hamiltonian matrix and its derivatives are inherently sparse, and taking this sparsity into account is crucial to make the SAME equations computationally manageable. The matrix structure can contain both sparse and dense matrices. Subroutines that implement the abstract matrix operations can choose internally the most appropriate algorithm according to the nature of the operands. For sparse matrix operations we have implemented our own algorithms that operate only on non-zero elements based on a simple coordinate storage format. This is not the most efficient approach, both in terms of the required storage and cache efficiency, but has the advantage of being simple. More sophisticated methods should be easy to implement. For all dense matrix operations, BLAS routines are used. Routines within the linear algebra module and other time consuming routines such as the construction of the Hamiltonian matrix have been parallelized using OpenMP directives.

The implementation of new tight binding models is a straightforward task, and only requires to add calls to particular subroutines to calculate the model-dependent radial hopping matrix elements, their derivatives and pair repulsion functions. These routines are easily plugged into a single interface module, and there is no need to modify any of the higher level routines. General routines for the calculation of the Slater-Koster factors and their derivatives have been implemented.

Equations of motion for the operators, such as $\hat{\rho}_e$ or the various $\hat{\mu}_\nu$, are integrated using the following "leapfrog" like method:

$$\hat{q}(t+\Delta t) = \hat{q}(t-\Delta t) + 2\Delta t \left.\frac{d\hat{q}}{dt}\right|_t$$

which is time reversible and unitary and therefore unconditionally stable. This simple integration scheme is extremely powerful. As an example, we have successfully performed Ehrenfest calculations (including self-consistency, which makes the Liouville equation nonlinear) for systems of thousands of atoms for many tens of femtoseconds using a time step of 0.01 femtoseconds. Particle numbers are conserved within numerical precision, and energy is conserved to a part in 10^9.

For an Ehrenfest calculation, the bottleneck is the calculation of the commutator $[\hat{H}, \hat{\rho}]$ which for a sparse Hamiltonian scales as M^2, where M is the number of basis functions. This makes Ehrenfest dynamics very competitive with Born-Oppenheimer dynamics. For large numbers of atoms, the better scaling compensates the fact that a hundred times smaller time step is needed, in a similar way to the Car-Parrinello method. Both the first-moment and second-moment dynamics have similar computational costs. The bottleneck in these cases is the calculation of products of the form $\hat{q}\hat{A}\hat{q}$, where $\hat{q}$ is $\hat{\rho}$ or $\hat{\mu}_{1,\nu}$ and $\hat{A}$ is a sparse operator. These terms appear in the equations of motion for the one-particle density matrices after the Hartree-Fock approximation is applied. In the present implementation, these are treated as dense-dense products, but in principle their scaling can be reduced to M^2. There are about N^2 of these products where N is the number of "quantum" ions.

3 Results

3.1 Joule heating

We present results for Joule heating of a single atom within a linear chain, using a first moment extension of the open boundary formalism described above. The tight binding model used was extremely simple: a chain of 1s atoms, with a hopping integral of -1eV 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 value of 0.648 eV. The variation with distance was a simple power law, with an exponent of 2 for the hopping integral and 4 for the repulsive potential. The device consists of nine atoms, the central atom of which is allowed to move (and whose quantum evolution is followed). The leads are 16 atoms long, and the integral for the environment covers only the most recent 7.5 fs. The initial electronic density matrix (which is also the reference density matrix for the environment) is found by diagonalising 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 have considered two slightly different systems: the first, with ordinary coupling between the central atom and the surrounding atoms; the second, with a weaker coupling (hopping integral of -0.5eV) for this atom only.

Before considering heating, we examine the current that results from application of a bias to this system. In Fig. 1(a) we see that a steady current is easily achieved after application of a bias (in all cases, the bias is applied to the left-hand lead and the left-hand side of the device by shifting the on-site terms in the Hamiltonian). There are two further important effects shown in Fig. 1(b): the effect of changing the coupling of the central atom to its neighbours and the effect of introducing classical kinetic energy to the central ion. The effect of weakening the coupling is, as expected, to reduce the current (though other effects will be explored below). The classical kinetic energy causes the ion to oscillate about its mean position: for the ordinary coupling at the ionic equilibrium position, current is a maximum as hopping into and out of the ion is equal, while at each extremum, current is a minimum as one of the two bonds to the nearest neighbours is significantly weakened. For the weak coupling, we see two further effects: first, the magnitude of the oscillations of the ionic position is smaller, resulting in smaller oscillations in the current; second, the

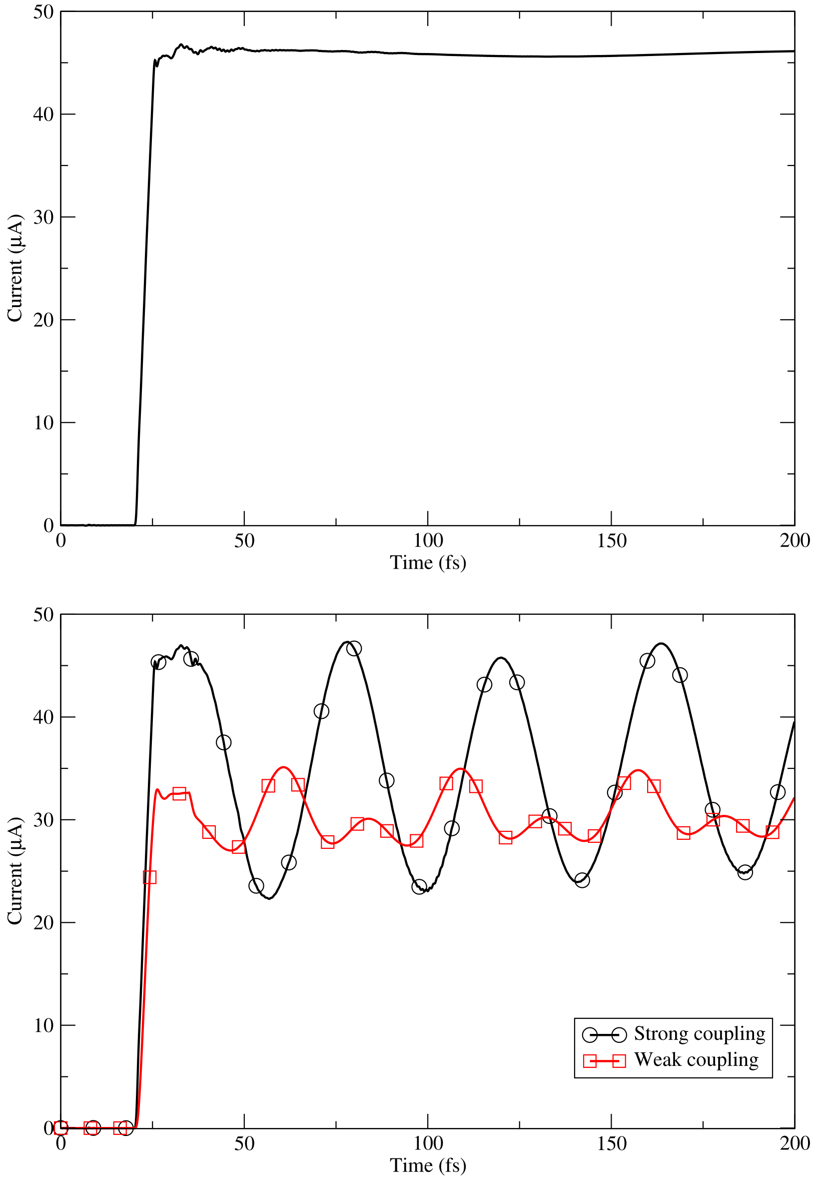

Figure 1: Current into central atom of chain when a bias of -0.6 V is applied at t =2 0 fs (linearly increased over 5 fs). (a) Ordinary coupling, no classical KE given to atom. (b) Ordinary and weak coupling with small classical KE given to the atom at 35 fs.

oscillations in the current show a doubling of the period and two separate height maxima relative to the ordinary coupling oscillations. This behaviour relates to the charging of the central ion at different extrema: when it is at the left-hand extremum (near the biased electrode) it loses charge to that electrode, so that when it reaches the mid-point, it has less charge than at equilibrium (i.e. zero bias) and the current is (relatively) large. When it is at the right-hand extremum it gains charge from the right-hand electrode, so that when it returns to the mid-point it has more charge than at equilibrium and the current is (relatively) small.

We now turn to heating, within the first moment approximation (i.e. retaining only $\hat{\mu}_{1,\nu}$ and $\hat{\lambda}_{1,\nu}$). The average kinetic energy now includes two terms, one arising from the average momentum of the ion, and the other from the qantum spread of momentum (we label these as "classical" and "quantum" contributions). These are plotted against time for the weak and ordinary coupling cases in Fig. 2, with classical KE in the top graph in each case, and quantum KE in the bottom graph. We see a number of important features: first, the classical kinetic energy decreases, as expected (electrons are being excited by the ions and removed from the open boundaries, leading to cooling); second, the quantum kinetic energy increases with bias and with time; third, the frequency of the classical kinetic energy oscillation increases with bias, due to a population of anti-bonding states as well as bonding states. The weakly coupled system exhibits higher frequency oscillations due to the weaker coupling; it also exhibits less heating *in the central ion* due to the lower current and weaker electronic correlations (in the limit of zero coupling, the heating goes to zero as expected).

3.2 Inelastic current-voltage spectroscopy

We will now show a direct calculation of inelastic current-voltage spectroscopy from second-moment CEID. The calculation is based on direct numerical integration of the full second-moment SAME equations of motion, with no approximation. Thus, this numerical calculation is inherently different, and superior, to the earlier analysis, based on the standard electron-phonon harmonic Hamiltonian expanded on a reference Born-Oppenheimer surface. We have a 131-atom metallic chain described by a tight binding-model with all parameters as in reference [11] except the ionic mass which is now 1 a.m.u. A single atom in the middle of the chain is allowed to move. A bias is applied, and a current flows, as in reference [11]. The current, for a given bias, is averaged over about one thermal vibration period. The current, differential conductance and its derivative with voltage are plotted against bias in figure 3.

The characteristic inelastic spectral feature (in the bottom panel) is clearly visible. The shoulder (bottom plot) beyond the voltage where the spectral feature occurs is the signature of the quantum heating of the ion that becomes activated at that critical voltage. This critical voltage, on the plot, is in excellent agreement with the value of $\hbar\omega = 0.26$ eV (where ω is the Born-Oppenheimer frequency of the ion), which may be expected on the basis of electron-phonon perturbation theory [14], and on the basis of the earlier

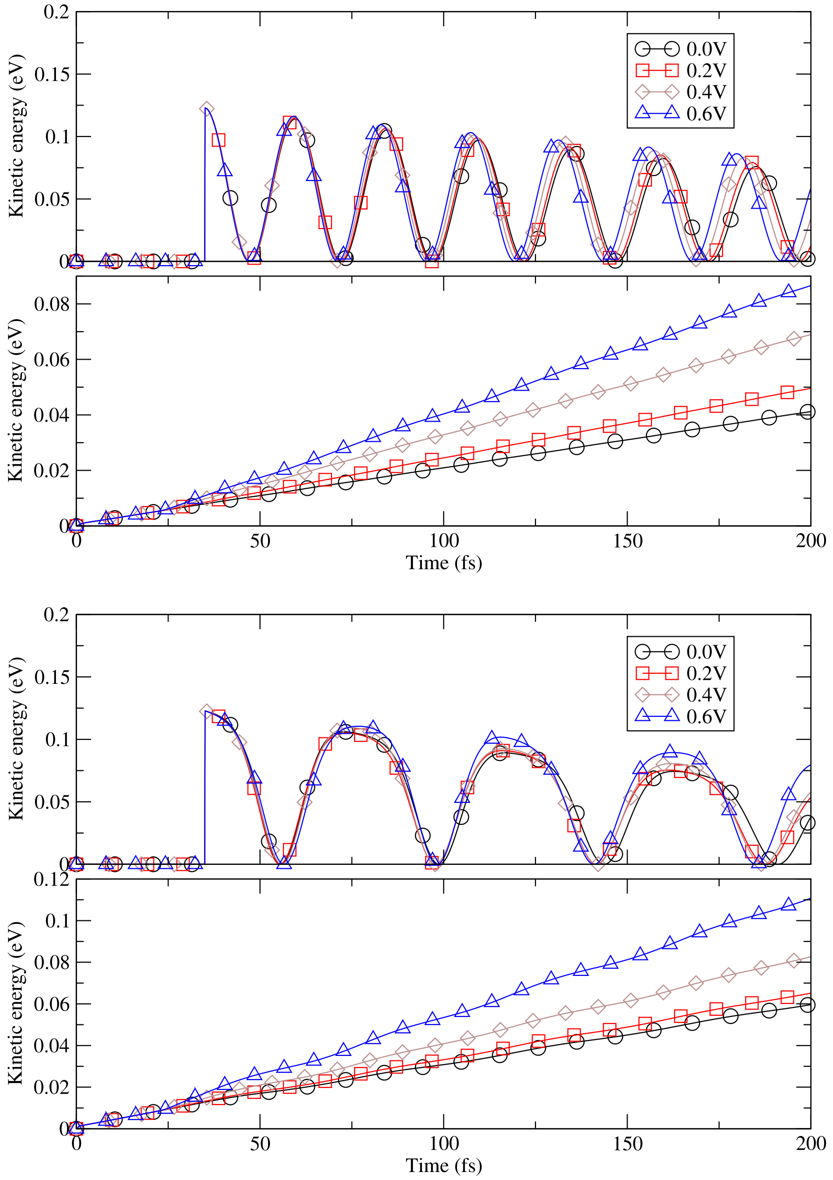

Figure 2: Classical (upper panels) and quantum (lower panels) KE for four biases: 0V, -0.2V, -0.4V and -0.6V. Bias applied at t=20fs (linearly increased over 5fs). A small classical KE was given to the atom at 35fs. Top graphs: Weak coupling. Bottom graphs: Ordinary coupling. Note the different energy scales for the quantum KE plots.

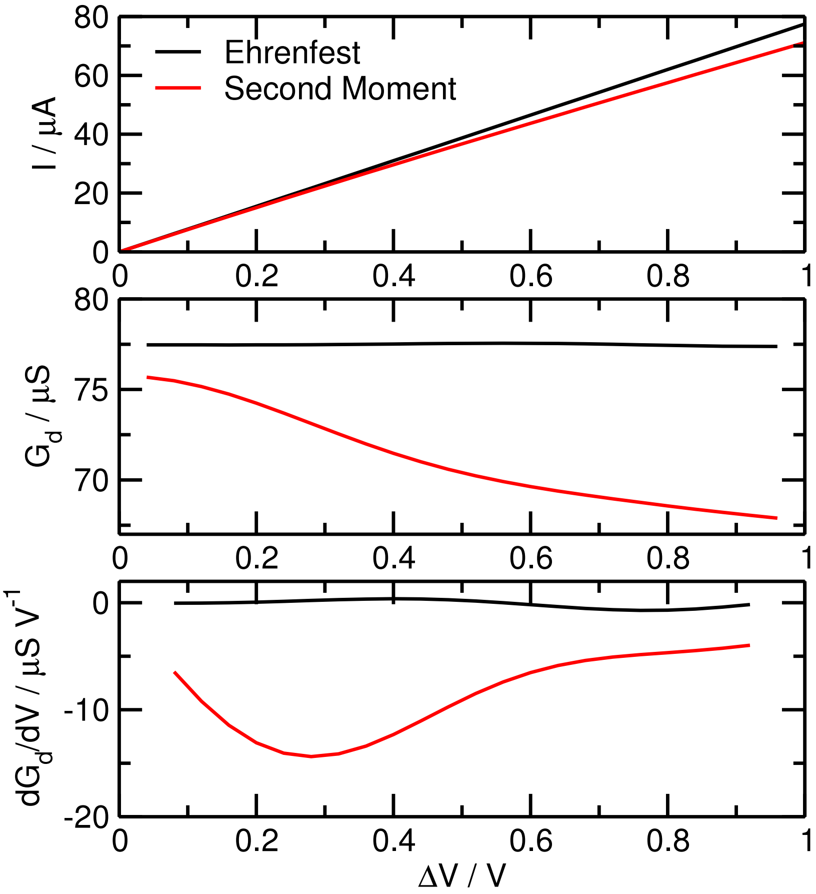

Figure 3: Current, differential conductance and its derivative with voltage, versus bias, for a single dynamical atom in a metallic chain.

analytical derivations. The physical origin of this feature is that for current carrying electrons to be able to excite vibrations, the excess electronic energy, set by the bias, has to exceed a phonon quantum. There is no other way to satisfy the selection rules for inelastic scattering, derived earlier. Hence, we expect inelastic scattering, the onset of dissipation and ionic heating, and a drop in conductance (due to the newly opened scattering mechanism) to occur at a bias that matches this phonon energy. And indeed it does. But, once again, the present simulations start from scratch and know nothing about any Born-Oppenheimer surfaces. Nor are the simulations constrained by the assumption of harmonicity, not are they perturbative. They furthermore allow phonons and electrons to be perturbed by each other in a consistent manner, both ways. In principle (though this is not done here) the method allows also the inclusion of electron-electron interactions and dynamical screening, at least in a Hartree-Fock, or in an adiabatic-LDA, spirit.

4 Conclusion and future directions

The range of problems to which this modelling technique can be applied is already large (ranging from low-energy I-V spectra to high-energy radiation damage) and we expect new and exciting insights to emerge as a result of this. However, the development of the formalism is not yet complete. The one qualitative feature left to work out is electron-electron correlation. We will begin at the mean-field level (Hartree-Fock or density functional theory). This is essential for describing (for example) the discharge of a capacitor. At the level of the Ehrenfest approximation this is straightforward and has already been implemented. Of course, if we could consider explicit two-electron correlation we should be able to model the onset of superconductivity in very small devices. This project, though, is for the more distant future.

A major area for which this approach is particularly well-suited is the transport of charge in biological systems. Biological systems have three important features that make conventional perturbative approaches difficult, but make a molecular dynamics based approach attractive:

1. They have very low symmetry in general, so many degrees of freedom need to be treated explicitly.
2. They are made from soft matter, so it is hard to define lattice sites about which oscillations occur. Indeed, diffusion can take place.
3. Calculations at zero temperature to define a reference state for the perturbation calculations could be qualitatively wrong, as biological systems make use of water, and water at low temperatures solidifies and behaves quite differently from the liquid at higher temperatures.

The presence of an environment that can contain charges clearly makes it important to introduce electrostatics into our equations of motion.

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