Correlated electron–ion dynamics: the excitation of atomic motion by energetic electrons

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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. This formalism is
extended here to include the explicit quantum spread of the ions and a
generalization of the Hartree–Fock approximation for incoherent sums of Slater
determinants. We demonstrate that the resultant dynamical equations reproduce
analytically the selection rules for inelastic electron–phonon scattering from
perturbation theory, which control the mutually driven excitations of the two
interacting subsystems. We then use CEID to make direct numerical simulations
of inelastic current–voltage spectroscopy in atomic wires, and to exhibit the
crossover from ionic cooling to heating as a function of the relative degree of
excitation of the electronic and ionic subsystems.

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 ionic 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 the 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 nonequilibrium 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 ions 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 that the energy separation between the surfaces is greater than $\hbar\omega$, where ω is a characteristic ionic vibrational frequency. This clearly eliminates all metals. But even then the effects are small because the ionic forces from each of the Born–Oppenheimer surfaces sampled are rather similar to one another. The lowest order corrections can be approximately included by means of a velocity dependent force that introduces the loss of energy of fast ions to the electrons [7], but this is negligible except for highly energetic ions.

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. Here we consider the irreversible exchange of energy between ions and current carrying electrons in atomic wires and the signature of these inelastic interactions in the current–voltage spectrum (Joule heating was considered in an earlier paper [8]). Conventional molecular dynamics cannot handle these problems, so we need to introduce modifications to capture them.

An approach used by a number of researchers when faced with these phenomena is the Ehrenfest approximation [9]. At the back of this is an exact set of results, namely the Ehrenfest *equations* [10], which read $\dot{\bar{R}}_\nu = \bar{P}_\nu/M_\nu$ and $\dot{\bar{P}}_\nu = \bar{F}_\nu$ where P_ν is a component of ionic momentum. While these look like the ordinary equations of Newtonian mechanics, they of course involve quantum expectation values: $\bar{R}_\nu = \langle\Psi|\hat{R}_\nu|\Psi\rangle$, $\bar{P}_\nu = \langle\Psi|\hat{P}_\nu|\Psi\rangle$, $\bar{F}_\nu = \langle\Psi|-\partial\hat{H}(\hat{R})/\partial\hat{R}_\nu|\Psi\rangle$, where $\hat{R}_\nu$ and $\hat{P}_\nu$ are ionic position and momentum operators satisfying the quantum commutation relation $[\hat{R}_\nu, \hat{P}_{\nu'}] = i\hbar\delta_{\nu\nu'}$,[5] and $\hat{H}(\hat{R})$ and $|\Psi\rangle$ are the Hamiltonian and wavefunction for the whole system of electrons and ions. We will often find it convenient to write $\hat{H}(\hat{R})$ as

$$\hat{H}(\hat{R}) = \hat{T}_I + \hat{H}_e(\hat{R}) \tag{1}$$

where $\hat{T}_I$ is the ionic kinetic energy operator and $\hat{H}_e$ contains everything else (the electronic kinetic energy, and the electron–electron, electron–ion and ion–ion interactions). The Ehrenfest *approximation* then makes an ansatz 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 $\hat{H}(\bar{R}) = \hat{T}_I + \hat{H}_e(\bar{R})$ produced by replacing the ionic position operator by its expectation value, and the full wavefunction $|\Psi\rangle$ is replaced by the electronic wavefunction $|\Phi\rangle$ which obeys $\hat{H}_e(\bar{R})|\Phi\rangle = i\hbar\partial|\Phi\rangle/\partial t$. 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 [11]).

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 nonadiabatic processes. But it clearly needs further extensions to reproduce many other nonadiabatic processes, notably the excitation of ionic motion by energetic electrons.

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[5] Square brackets denote a commutator: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

In this paper we present a method that describes electron–ion correlations, inelastic electron–phonon interactions and the resultant energy exchange between the two subsystems, while remaining, at the same time, a form of molecular dynamics. In the next section we describe this formalism—the second-moment approximation to the small amplitude moment expansion (SAME)—and then explain its properties in terms of a trajectory interpretation of quantum mechanics. In the subsequent section this method for correlated electron–ion molecular dynamics is compared with standard electron–phonon scattering theory. Finally we give numerical dynamical simulations of mutually driven electron–phonon excitations in an atomic wire and of their signature in the transport properties of the wire. The time per molecular dynamics time step (typically 0.01 fs) for a simulation with M atomic orbitals and N mobile atoms is $\tau \times M^2 \times N^2$, where τ is a machine dependent constant. On a single processor using current hardware, $\tau \approx 25 \ \mu$s.

2. The second-moment equations

2.1. Many-body equations

Our strategy for extending molecular dynamics to include correlations between electrons and ions has been discussed in detail before [8]. Here we just outline the approach, and give the key 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 $\Delta \hat{R}_\nu = \hat{R}_\nu - \bar{R}_\nu$. 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 $\hat{\rho}_e = \text{Tr}_I\{\hat{\rho}\}$ where $\text{Tr}_I\{\star\}$ means a trace over ionic coordinates. In a real space representation this would be $\hat{\rho}_e = \int d\vec{R} \langle \vec{R}|\hat{\rho}|\vec{R}\rangle$. The equation of motion is the quantum Liouville equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]. \tag{2}$$

This equation of motion is the foundation of our approach. Using equation (1), the Ehrenfest approximation can be written as

$$\dot{\bar{R}}_\nu = \frac{\bar{P}_\nu}{M_\nu} \qquad \dot{\bar{P}}_\nu = \bar{F}_\nu$$

$$\bar{F}_\nu = \text{Tr}_e\left\{\hat{\rho}_e\left(-\frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}_\nu}\right)\right\} \qquad i\hbar \frac{\partial \hat{\rho}_e}{\partial t} = \left[\hat{H}_e(\bar{R}), \hat{\rho}_e\right] \tag{3}$$

where $\text{Tr}_e\{\star\}$ means a trace over electronic degrees of freedom. Note that if we define the Ehrenfest energy by $E_{\text{Ehrenfest}} = \sum_\nu \bar{P}_\nu^2/2M_\nu + \text{Tr}_e\{\hat{\rho}_e \hat{H}_e(\bar{R})\}$ 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 ions are well defined by classical trajectories ($\bar{R}_\nu$) but that these are slightly broadened (by characteristic amounts $\overline{\Delta R_\nu^2}$) because of the quantum nature of the ions.

Consider first the effective force $\bar{F}_\nu$. According to the Ehrenfest equations (*not* approximation) this is given by $\bar{F}_\nu = -\text{Tr}\{\hat{\rho} \, \partial \hat{H}_e(\hat{R})/\partial \hat{R}_\nu\}$. For small fluctuations about the mean trajectory $\bar{R}$ we can make a Taylor expansion to get

$$\bar{F}_\nu = \text{Tr}\left\{\hat{\rho}\left(-\frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}_\nu} - \sum_{\nu'} \frac{\partial^2 \hat{H}_e(\bar{R})}{\partial \bar{R}_\nu \partial \bar{R}_{\nu'}}\Delta \hat{R}_{\nu'} - \frac{1}{2}\sum_{\nu'\nu''} \frac{\partial^3 \hat{H}_e(\bar{R})}{\partial \bar{R}_\nu \partial \bar{R}_{\nu'} \partial \bar{R}_{\nu''}}\Delta \hat{R}_{\nu'}\Delta \hat{R}_{\nu''} + \cdots\right)\right\}$$

$$= \text{Tr}_e\{\hat{\rho}_e \hat{F}_\nu\} - \sum_{\nu'} \text{Tr}_e\{\hat{K}_{2,\nu\nu'}\hat{\mu}_{1,\nu'}\} - \frac{1}{2}\sum_{\nu'\nu''} \text{Tr}_e\{\hat{K}_{3,\nu\nu'\nu''}\hat{\mu}_{2,\nu'\nu''}\} + \cdots \tag{4}$$

where we have introduced the force operator $\hat{F}_\nu = -\partial \hat{H}_e(\bar{R})/\partial \bar{R}_\nu$, the spring operator $\hat{K}_{2,\nu\nu'} = \partial^2 \hat{H}_e(\bar{R})/\partial \bar{R}_\nu \partial \bar{R}_{\nu'}$, the anharmonic spring operator $\hat{K}_{3,\nu\nu'\nu''} = \partial^3 \hat{H}_e(\bar{R})/\partial \bar{R}_\nu \partial \bar{R}_{\nu'} \partial \bar{R}_{\nu''}$ and the moment operators $\hat{\mu}_{1,\nu} = \text{Tr}_I\{\Delta \hat{R}_\nu \hat{\rho}\}$ and $\hat{\mu}_{2,\nu\nu'} = \text{Tr}_I\{\Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \hat{\rho}\}$. In general the moments measure the ionic distribution [12–14] as a function of electronic state. We provide a more intuitive interpretation later on.

The question of how far to take the Taylor expansion now arises. Previously we stopped at the first moment $\hat{\mu}_{1,\nu}$ [8]. However, this does not allow us to introduce the explicit quantum width of the ions. For this we need to go at least as far as $\hat{\mu}_{2,\nu\nu'}$, as the width involves $\Delta \hat{R}_\nu^2$. In this work we stop at this level (the second moment).

To evaluate the force we need to determine the electron density matrix and moments, which we can find by integrating their equations of motion. The equation of motion for a general moment defined by $\hat{q} = \text{Tr}_I\{\hat{\rho}\hat{Q}(\Delta \hat{R}, \Delta \hat{P})\}$, where $\Delta \hat{P}_\nu = \hat{P}_\nu - \bar{P}_\nu$ and $\hat{Q}$ is an ionic operator, is [8]

$$
\begin{aligned}
\frac{\partial \hat{q}}{\partial t} = \text{Tr}_I &\left\{ \sum_\nu \left(\frac{\bar{P}_\nu}{M_\nu} \frac{\partial \hat{Q}}{\partial \bar{R}_\nu} + \bar{F}_\nu \frac{\partial \hat{Q}}{\partial \bar{P}_\nu} \right) \hat{\rho} \right\} + \frac{1}{i\hbar} \text{Tr}_I\{\hat{Q}[\hat{H}, \hat{\rho}]\} \\
= &\sum_\nu \frac{1}{2M_\nu} \text{Tr}_I \left\{ \left(\Delta \hat{P}_\nu \frac{\partial \hat{Q}}{\partial \Delta \hat{R}_\nu} + \frac{\partial \hat{Q}}{\partial \Delta \hat{R}_\nu} \Delta \hat{P}_\nu \right) \hat{\rho} \right\} - \sum_\nu \bar{F}_\nu \text{Tr}_I \left\{ \frac{\partial \hat{Q}}{\partial \Delta \hat{P}_\nu} \hat{\rho} \right\} \\
&+ \frac{1}{i\hbar} \left[\hat{H}_e(\bar{R}), \hat{q} \right] - \frac{1}{i\hbar} \sum_\nu \left[\hat{F}_\nu, \text{Tr}_I \left\{ \frac{1}{2} \left(\hat{Q} \Delta \hat{R}_\nu + \Delta \hat{R}_\nu \hat{Q} \right) \hat{\rho} \right\} \right] \\
&- \frac{1}{i\hbar} \sum_\nu \frac{1}{2} \left(\hat{F}_\nu \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu]\hat{\rho}\} + \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu]\hat{\rho}\} \hat{F}_\nu \right) \\
&+ \frac{1}{i\hbar} \frac{1}{2} \sum_{\nu\nu'} \left[\hat{K}_{2,\nu\nu'}, \text{Tr}_I \left\{ \frac{1}{2} \left(\hat{Q} \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} + \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \hat{Q} \right) \hat{\rho} \right\} \right] \\
&+ \frac{1}{i\hbar} \frac{1}{2} \sum_{\nu\nu'} \frac{1}{2} \left(\hat{K}_{2,\nu\nu'} \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'}]\hat{\rho}\} + \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'}]\hat{\rho}\} \hat{K}_{2,\nu\nu'} \right) \\
&+ \frac{1}{i\hbar} \frac{1}{6} \sum_{\nu\nu'\nu''} \left[\hat{K}_{3,\nu\nu'\nu''}, \text{Tr}_I \left\{ \frac{1}{2} \left(\hat{Q} \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \Delta \hat{R}_{\nu''} + \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \Delta \hat{R}_{\nu''} \hat{Q} \right) \hat{\rho} \right\} \right] \\
&+ \frac{1}{i\hbar} \frac{1}{6} \sum_{\nu\nu'\nu''} \frac{1}{2} \left(\hat{K}_{3,\nu\nu'\nu''} \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \Delta \hat{R}_{\nu''}]\hat{\rho}\} \right. \\
&\left. + \text{Tr}_I\{[\hat{Q}, \Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \Delta \hat{R}_{\nu''}]\hat{\rho}\} \hat{K}_{3,\nu\nu'\nu''} \right) + \cdots.
\end{aligned} \tag{5}
$$

We have found that we can reduce the number of equations of motion we have to integrate, while not losing accuracy, by using the following ansatz for the second moment:

$$
\hat{\mu}_{2,\nu\nu'} = C_{\nu\nu'}^{RR} \hat{\rho}_e \tag{6}
$$

where $C_{\nu\nu'}^{RR} = \text{Tr}\{\Delta \hat{R}_\nu \Delta \hat{R}_{\nu'} \hat{\rho}\}$. This expression will be analysed further in a later paper in which we will study the truncation of the moment expansion, but for now we offer the following justification.

There are in fact two expansion parameters in our problem: ionic fluctuations (IF) and electron–ion correlations (EIC). To distinguish between them, consider first a quantum ion sliding in a static potential landscape, such as a given Born–Oppenheimer surface. This scenario allows an arbitrary degree of quantum ionic fluctuations (with infinitely many nontrivial moments and, in particular, with ionic zero-point motion), but zero EIC. Of course, the Born–Oppenheimer approximation does involve correlation between ions and the electron

gas, but these occur at the level of the response of the *mean electron density* to the ionic motion (as opposed to correlations between ions with individual electrons), and this is, therefore, still a mean field approximation, with zero EIC in our sense of the term. By contrast, an essentially classical ion (with, for instance, no zero-point motion) can still correlate with electrons and irreversibly exchange energy with them in inelastic interactions, as is demonstrated by the first-moment expansion of correlated electron–ion dynamics (CEID) [8], as well as by pure classical mechanics, applied in a consistent manner to electrons and ions [11]. Equation (6) *looks like* an application of the mean field approximation $\hat{\rho} = \hat{\rho}_e \otimes \hat{\rho}_I$, where $\hat{\rho}_I$ is an ionic density matrix. However, it actually constitutes a consistent scheme for truncating our equations to lowest nontrivial order in EIC (first order, as measured by $\hat{\mu}_1$, and the analogous quantity for momentum fluctuations, $\hat{\lambda}_1$, defined below) and to lowest nontrivial order in IF (second order, as measured by $\overline{\Delta R^2} = C^{RR}$, and the analogous quantities C^{PR} and C^{PP} for momentum–position and momentum–momentum fluctuations, defined below, with $\overline{\Delta R} = 0$, $\overline{\Delta P} = 0$). Indeed, writing, at the next level, $\hat{\mu}_2 = \text{Tr}_I\{\Delta \hat{R}^2[\hat{\rho}_e \otimes \hat{\rho}_I + \mathcal{O}(\hat{\mu}_1, \hat{\lambda}_1)]\}$ overall invokes effects at the level of $\Delta \hat{R}^3$ and falls beyond our present considerations. The consistent truncation of SAME to order higher than 1 in EIC and to order higher than 2 in IF is the subject of ongoing research.

In view of equation (6), the effective force in equation (4) changes to

$$\bar{F}_\nu = \text{Tr}_e\left\{\hat{\rho}_e \hat{F}_\nu\right\} - \sum_{\nu'} \text{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\hat{\mu}_{1,\nu'}\right\} - \tfrac{1}{2}\sum_{\nu'\nu''} C^{RR}_{\nu'\nu''} \text{Tr}_e\left\{\hat{K}_{3,\nu\nu'\nu''}\hat{\rho}_e\right\}. \tag{7}$$

The remaining equations of motion for the moments are

$$\frac{\partial \hat{\rho}_e}{\partial t} = \frac{1}{i\hbar}\left[\hat{H}_e(\bar{R}), \hat{\rho}_e\right] - \frac{1}{i\hbar}\sum_\nu\left[\hat{F}_\nu, \hat{\mu}_{1,\nu}\right] + \frac{1}{i\hbar}\frac{1}{2}\sum_{\nu\nu'} C^{RR}_{\nu\nu'}\left[\hat{K}_{2,\nu\nu'}, \hat{\rho}_e\right]$$

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

$$\frac{\partial \hat{\lambda}_{1,\nu}}{\partial t} = \frac{1}{i\hbar}\left[\hat{H}_e(\bar{R}), \hat{\lambda}_{1,\nu}\right] - \frac{1}{i\hbar}\sum_{\nu'} C^{PR}_{\nu\nu'}\left[\hat{F}_{\nu'}, \hat{\rho}_e\right] + \frac{1}{2}\left(\Delta\hat{F}_\nu\hat{\rho}_e + \hat{\rho}_e\Delta\hat{F}_\nu\right)$$

$$\qquad - \sum_{\nu'}\tfrac{1}{2}\left(\hat{K}_{2,\nu\nu'}\hat{\mu}_{1,\nu'} + \hat{\mu}_{1,\nu'}\hat{K}_{2,\nu\nu'}\right)$$

$$\qquad - \tfrac{1}{2}\sum_{\nu'\nu''}\tfrac{1}{2}C^{RR}_{\nu'\nu''}\left(\hat{K}_{3,\nu\nu'\nu''}\hat{\rho}_e + \hat{\rho}_e\hat{K}_{3,\nu\nu'\nu''}\right) \tag{8}$$

where we have introduced the further moment $\hat{\lambda}_{1,\nu} = \text{Tr}_I\{\Delta\hat{P}_\nu\hat{\rho}\}$ and the analogue of equation (6):

$$\hat{\chi}_{2,\nu\nu'} = \tfrac{1}{2}\text{Tr}_I\left\{\left(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu\right)\hat{\rho}\right\} \approx C^{PR}_{\nu\nu'}\hat{\rho}_e \tag{9}$$

with $C^{PR}_{\nu\nu'} = \tfrac{1}{2}\text{Tr}\{(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu)\hat{\rho}\}$, and we have defined $\Delta\hat{F}_\nu = \hat{F}_\nu - \bar{F}_\nu$.

Once again, the truncation of the equations of motion is the subject of ongoing work. The present scheme, whose philosophy was discussed above, has the important advantage that it enables us to construct a strictly conserved energy. The second-moment energy reads

$$E_2 = \sum_\nu \frac{1}{2M_\nu}\left(\bar{P}_\nu^2 + C^{PP}_{\nu\nu}\right) + \text{Tr}_e\left\{\hat{\rho}_e\hat{H}_e(\bar{R})\right\}$$

$$\qquad - \sum_\nu \text{Tr}_e\left\{\hat{F}_\nu\hat{\mu}_{1,\nu}\right\} + \tfrac{1}{2}\sum_{\nu\nu'} \text{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\hat{\mu}_{2,\nu'\nu}\right\} \tag{10}$$

where $C_{\nu\nu'}^{PP} = \text{Tr}\{\Delta\hat{P}_\nu\Delta\hat{P}_{\nu'}\hat{\rho}\}$. However, in the presence of relations (6) and (9), in order to obtain a conserved energy it is necessary to first differentiate the last term above with respect to time, invoke these relations in the derivative and then integrate back, which yields

$$E_2 = \sum_\nu \frac{1}{2M_\nu}\left(\bar{P}_\nu^2 + C_{\nu\nu}^{PP}\right) + \text{Tr}_e\left\{\hat{\rho}_e\hat{H}_e(\bar{R})\right\} - \sum_\nu \text{Tr}_e\left\{\hat{F}_\nu\hat{\mu}_{1,\nu}\right\} + \int^t w_K(t')\,dt' \tag{11}$$

where

$$w_K = \frac{1}{2}\sum_{\nu\nu'\nu''} C_{\nu'\nu}^{RR}\,\text{Tr}_e\left\{\hat{K}_{3,\nu\nu'\nu''}\hat{\rho}_e\right\}\frac{\bar{P}_{\nu''}}{M_{\nu''}} + \sum_{\nu\nu'}\text{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\hat{\rho}_e\right\}\frac{C_{\nu\nu'}^{PR}}{M_\nu}$$

$$+ \frac{1}{2i\hbar}\sum_{\nu\nu'} C_{\nu'\nu}^{RR}\,\text{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\left[\hat{H}_e(\bar{R}),\hat{\rho}_e\right]\right\}. \tag{12}$$

The energy in equation (11) is a constant of the motion under equations (7), (8) and (13) below. Equation (11) furthermore has the property that the consistent neglect of all terms in $\hat{K}_3$ leaves energy conservation unaffected. Indeed, in the numerical results to be presented later, $\hat{K}_3$ has been neglected, since at thermal ionic energies its contributions to the equations of motion are tiny.

To obtain closure we need equations of motion for $C_{\nu\nu'}^{RR}$ and $C_{\nu\nu'}^{PR}$. These are obtained from the equations of motion of the corresponding moments by taking a trace over electronic degrees of freedom (for example, $C_{\nu\nu'}^{RR} = \text{Tr}_e\{\hat{\mu}_{2,\nu\nu'}\}$; hence $\partial C_{\nu\nu'}^{RR}/\partial t = \text{Tr}_e\{\partial\hat{\mu}_{2,\nu\nu'}/\partial t\}$), and we thus have

$$\frac{\partial C_{\nu\nu'}^{RR}}{\partial t} = \frac{C_{\nu\nu'}^{PR}}{M_\nu} + \frac{C_{\nu'\nu}^{PR}}{M_{\nu'}}$$

$$\frac{\partial C_{\nu\nu'}^{PR}}{\partial t} = \frac{C_{\nu\nu'}^{PP}}{M_{\nu'}} + \text{Tr}_e\left\{\hat{F}_\nu\hat{\mu}_{1,\nu'}\right\} - \sum_{\nu''}\bar{K}_{2,\nu\nu''}C_{\nu''\nu'}^{RR} \tag{13}$$

$$\frac{\partial C_{\nu\nu'}^{PP}}{\partial t} = \text{Tr}_e\left\{\hat{F}_\nu\hat{\lambda}_{1,\nu'} + \hat{\lambda}_{1,\nu}\hat{F}_{\nu'}\right\} - \sum_{\nu''}\left(C_{\nu\nu''}^{PR}\bar{K}_{2,\nu''\nu'} + \bar{K}_{2,\nu''\nu}C_{\nu'\nu''}^{PR}\right)$$

where $\bar{K}_{2,\nu\nu'} = \text{Tr}_e\{\hat{K}_{2,\nu\nu'}\hat{\rho}_e\}$.

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 one-electron matrices by tracing out all but one electron [8]. To produce closure we make a Hartree–Fock approximation for two-electron matrices. However, since in the presence of electron–ion correlations the one-particle density matrix is not in general idempotent even for noninteracting electrons, we need to augment the usual result. This we now do.

2.2. The extended Hartree–Fock approximation

The electron density matrix is defined by

$$\hat{\rho}_e = \int d\vec{R}\,\langle\vec{R}|\hat{\rho}|\vec{R}\rangle = \int d\vec{R}\,\tilde{\rho}_e(\vec{R})\rho_I(\vec{R}) \tag{14}$$

where $\tilde{\rho}_e(\vec{R}) = \langle\vec{R}|\hat{\rho}|\vec{R}\rangle/\rho_I(\vec{R})$ and $\rho_I(\vec{R}) = \text{Tr}_e\{\langle\vec{R}|\hat{\rho}|\vec{R}\rangle\}$. We now generate related matrices

$$\hat{\rho}_e^{(1)} = \text{Tr}_{e,2\ldots N}\left\{\hat{\rho}_e\right\} = \int d\vec{R}\,\tilde{\rho}_e^{(1)}(\vec{R})\rho_I(\vec{R}) \tag{15}$$

$$\hat{\mu}_{1,\nu}^{(1)} = \text{Tr}_{e,2\ldots N}\left\{\hat{\mu}_{1,\nu}\right\} = \int d\vec{R}\,\Delta R_\nu\tilde{\rho}_e^{(1)}(\vec{R})\rho_I(\vec{R}) \tag{16}$$

$$\hat{\rho}_{e}^{(2)} = \mathrm{Tr}_{e,3\ldots N}\left\{\hat{\rho}_{e}\right\} = \int d\vec{R}\, \tilde{\rho}_{e}^{(2)}(\vec{R})\rho_{I}(\vec{R}) \tag{17}$$

where $\hat{\rho}_{e}^{(1)}$ and $\tilde{\rho}_{e}^{(1)}$ are the one-electron density matrices, $\hat{\rho}_{e}^{(2)}$ and $\tilde{\rho}_{e}^{(2)}$ are two-electron density matrices and $\hat{\mu}_{1,\nu}^{(1)}$ is the one-electron first moment. By $\mathrm{Tr}_{e,n\ldots N}\{\star\}$ we mean a trace over electrons n to N. Because of the narrowness of $\rho_{I}(\vec{R})$ about $\bar{R}$ we can make the following Taylor expansions:

$$\hat{\rho}_{e}^{(1)} = \int d\vec{R}\left(\tilde{\rho}_{e}^{(1)}(\bar{R}) + \sum_{\nu}\Delta R_{\nu}\tilde{\rho}_{e,\nu}^{(1)}(\bar{R}) + \tfrac{1}{2}\sum_{\nu\nu'}\Delta R_{\nu}\Delta R_{\nu'}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R}) + \cdots\right)\rho_{I}(\vec{R})$$

$$= \tilde{\rho}_{e}^{(1)}(\bar{R}) + \tfrac{1}{2}\sum_{\nu\nu'}C_{\nu\nu'}^{RR}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R}) + \cdots \tag{18}$$

$$\hat{\mu}_{1,\nu}^{(1)} = \int d\vec{R}\,\Delta R_{\nu}\left(\tilde{\rho}_{e}^{(1)}(\bar{R}) + \sum_{\nu'}\Delta R_{\nu'}\tilde{\rho}_{e,\nu'}^{(1)}(\bar{R}) + \cdots\right)\rho_{I}(\vec{R})$$

$$= \sum_{\nu'}C_{\nu\nu'}^{RR}\tilde{\rho}_{e,\nu'}^{(1)}(\bar{R}) + \cdots \tag{19}$$

where $\tilde{\rho}_{e,\nu}^{(1)}(\bar{R}) = \partial\tilde{\rho}_{e}^{(1)}(\bar{R})/\partial\bar{R}_{\nu}$, $\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R}) = \partial^{2}\tilde{\rho}_{e}^{(1)}(\bar{R})/\partial\bar{R}_{\nu}\partial\bar{R}_{\nu'}$ and $C_{\nu\nu'}^{RR} = \int d\vec{R}\,\Delta R_{\nu}\Delta R_{\nu'}\rho_{I}(\vec{R})$, and we have made use of the normalization $\int d\vec{R}\,\rho_{I}(\vec{R}) = 1$ and the definition $\int d\vec{R}\,\Delta R_{\nu}\rho_{I}(\vec{R}) = 0$. Thus we get

$$\tilde{\rho}_{e,\nu}^{(1)}(\bar{R}) = \sum_{\nu'}D_{\nu\nu'}^{RR}\hat{\mu}_{1,\nu'}^{(1)} + \cdots \tag{20}$$

where $\sum_{\nu''}D_{\nu\nu''}^{RR}C_{\nu''\nu'}^{RR} = \delta_{\nu\nu'}$ (that is, $D_{\nu\nu'}^{RR}$ is the inverse matrix of $C_{\nu\nu'}^{RR}$). We now make the usual Hartree–Fock approximation for $\tilde{\rho}_{e}^{(2)}(\bar{R})$ in equation (17). For this we need to move from operator to matrix notation. We define the elements of a one-particle matrix $O^{(1)}(1;1')$ by $O^{(1)}(1;1') = \langle 1|\hat{O}^{(1)}|1'\rangle$, where the set of states $\{|1\rangle\}$ spans the space available to electron 1. Similarly, for a two-particle matrix we have $O^{(2)}(12;1'2') = \langle 12|\hat{O}^{(1)}|1'2'\rangle$. The Hartree–Fock approximation is $\rho_{e}^{(2,\mathrm{HF})}(12;1'2') = \rho_{e}^{(1)}(1;1')\rho_{e}^{(1)}(2;2') - \rho_{e}^{(1)}(1;2')\rho_{e}^{(1)}(2;1')$, which allows us to write

$$\rho_{e}^{(2)}(12;1'2') \approx \int d\vec{R}\,\rho_{I}(\vec{R})\left(\tilde{\rho}_{e}^{(1)}(\vec{R};11')\tilde{\rho}_{e}^{(1)}(\vec{R};22') - \tilde{\rho}_{e}^{(1)}(\vec{R};12')\tilde{\rho}_{e}^{(1)}(\vec{R};21')\right)$$

$$= \int d\vec{R}\,\rho_{I}(\vec{R})\Bigg(\bigg(\tilde{\rho}_{e}^{(1)}(\bar{R};11') + \sum_{\nu}\Delta R_{\nu}\tilde{\rho}_{e,\nu}^{(1)}(\bar{R};11')$$

$$+ \tfrac{1}{2}\sum_{\nu\nu'}\Delta R_{\nu}\Delta R_{\nu'}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R};11') + \cdots\bigg)\bigg(\tilde{\rho}_{e}^{(1)}(\bar{R};22') + \sum_{\nu}\Delta R_{\nu}\tilde{\rho}_{e,\nu}^{(1)}(\bar{R};22')$$

$$+ \tfrac{1}{2}\sum_{\nu\nu'}\Delta R_{\nu}\Delta R_{\nu'}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R};22') + \cdots\bigg) - \bigg(\tilde{\rho}_{e}^{(1)}(\bar{R};12') + \sum_{\nu}\Delta R_{\nu}\tilde{\rho}_{e,\nu}^{(1)}(\bar{R};12')$$

$$+ \tfrac{1}{2}\sum_{\nu\nu'}\Delta R_{\nu}\Delta R_{\nu'}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R};12') + \cdots\bigg)\bigg(\tilde{\rho}_{e}^{(1)}(\bar{R};21') + \sum_{\nu}\Delta R_{\nu}\tilde{\rho}_{e,\nu}^{(1)}(\bar{R};21')$$

$$+ \tfrac{1}{2}\sum_{\nu\nu'}\Delta R_{\nu}\Delta R_{\nu'}\tilde{\rho}_{e,\nu\nu'}^{(1)}(\bar{R};21') + \cdots\bigg)\Bigg)$$

$$= \rho_{e}^{(1)}(11')\rho_{e}^{(1)}(22') - \rho_{e}^{(1)}(12')\rho_{e}^{(1)}(21') + \sum_{\nu\nu'}C_{\nu\nu'}^{RR}\big(\tilde{\rho}_{e,\nu}^{(1)}(\bar{R};11')\tilde{\rho}_{e,\nu'}^{(1)}(\bar{R};22')$$

$$- \tilde{\rho}_{e,\nu}^{(1)}(\bar{R};12')\tilde{\rho}_{e,\nu'}^{(1)}(\bar{R};21')\big) + \cdots$$

$$= \rho_{\mathrm{e}}^{(1)}(11')\rho_{\mathrm{e}}^{(1)}(22') - \rho_{\mathrm{e}}^{(1)}(12')\rho_{\mathrm{e}}^{(1)}(21')$$
$$+ \sum_{\nu\nu'} D_{\nu\nu'}^{RR} \left(\mu_{1,\nu'}^{(1)}(11')\mu_{1,\nu}^{(1)}(22') - \mu_{1,\nu'}^{(1)}(12')\mu_{1,\nu}^{(1)}(21') \right) + \cdots. \tag{21}$$

Using the normalization convention $(N-1)\hat{\rho}_{\mathrm{e}}^{(1)} = \mathrm{Tr}_{\mathrm{e},2}\{\hat{\rho}_{\mathrm{e}}^{(2)}\}$ we get

$$\hat{\rho}_{\mathrm{e}}^{(1)} = \hat{\rho}_{\mathrm{e}}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} + \sum_{\nu\nu'} D_{\nu\nu'}^{RR} \hat{\mu}_{1,\nu'}^{(1)}\hat{\mu}_{1,\nu}^{(1)} \tag{22}$$

which is the generalization of the usual idempotency condition. Note that this new condition respects fermionicity provided that $D_{\nu\nu'}^{RR}$ is positive definite. The Hartree–Fock approximations for the moments are exactly as published previously [8] provided that we retain only terms up to those quadratic in the fluctuations.

2.3. One-particle second-moment equations

Once all the electrons except one have been traced out, and the Hartree–Fock approximation used to express two-electron matrices in terms of one-electron matrices [8], we get the following equations. The total energy is

$$E_2 = \frac{1}{2}\sum_{\nu}\frac{1}{M_\nu}\left(\bar{P}_\nu^2 + C_{\nu\nu}^{PP}\right) + \hat{H}_{\mathrm{e}}^{(0)}(\bar{R}) + \mathrm{Tr}_{\mathrm{e},1}\left\{\hat{\rho}_{\mathrm{e}}^{(1)}\left(\hat{H}_{\mathrm{e}}^{(\mathrm{HF})} - \frac{1}{2}\hat{J}_{\mathrm{e}}^{(\mathrm{HF})}\right)\right\}$$
$$- \sum_{\nu}\mathrm{Tr}_{\mathrm{e},1}\left\{\hat{F}_\nu^{(1)}\hat{\mu}_{1,\nu}^{(1)}\right\} + \frac{1}{2}\sum_{\nu\nu'}D_{\nu\nu'}^{RR}\mathrm{Tr}_{\mathrm{e},1}\left\{\hat{\mu}_{1,\nu'}^{(1)}\hat{J}_{\mu_{1,\nu}}^{(\mathrm{HF})}\right\} + \int^t w_K(t')\,\mathrm{d}t'$$

where $\hat{H}_{\mathrm{e}}^{(\mathrm{HF})} = \hat{H}_{\mathrm{e}}^{(1)} + \hat{J}_{\mathrm{e}}^{(\mathrm{HF})}$ is the Fock matrix and

$$J_{\mathrm{e}}^{(\mathrm{HF})}(1,1') = \sum_{22'}\left(H_{\mathrm{e}}^{(2)}(12,1'2') - H_{\mathrm{e}}^{(2)}(12,2'1')\right)\rho^{(1)}(2',2) \tag{23}$$

is the mean field two-electron contribution to the energy (Hartree plus exchange) and

$$J_{\mu_{1,\nu}}^{(\mathrm{HF})}(1,1') = \sum_{22'}\left(H_{\mathrm{e}}^{(2)}(12,1'2') - H_{\mathrm{e}}^{(2)}(12,2'1')\right)\mu_{1,\nu}^{(1)}(2',2) \tag{24}$$

is the correction due to correlations between electrons and ions, and now

$$w_K = \frac{1}{2}\sum_{\nu\nu'\nu''}C_{\nu'\nu}^{RR}\left(\hat{K}_{3,\nu\nu'\nu''}^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\left\{\hat{K}_{3,\nu\nu'\nu''}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}\right\}\right)\frac{\bar{P}_{\nu''}}{M_{\nu''}}$$
$$+ \sum_{\nu\nu'}\left(\hat{K}_{2,\nu\nu'}^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\left\{\hat{K}_{2,\nu\nu'}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}\right\}\right)\frac{C_{\nu\nu'}^{PR}}{M_\nu} + \frac{1}{2\mathrm{i}\hbar}$$
$$\times \sum_{\nu\nu'}C_{\nu'\nu}^{RR}\mathrm{Tr}_{\mathrm{e}}\left\{\hat{K}_{2,\nu\nu'}^{(1)}\left(\left[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})},\hat{\rho}_{\mathrm{e}}^{(1)}\right] + \sum_{\nu''\nu'''}D_{\nu''\nu'''}^{RR}\left[\hat{J}_{\mu_{1,\nu''}}^{(\mathrm{HF})},\hat{\mu}_{1,\nu'''}^{(1)}\right]\right)\right\}. \tag{25}$$

The effective ionic force is

$$\bar{F}_\nu = \hat{F}_\nu^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\left\{\hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_\nu^{(1)}\right\} - \sum_{\nu'}\mathrm{Tr}_{\mathrm{e},1}\left\{\hat{K}_{2,\nu\nu'}^{(1)}\hat{\mu}_{1,\nu'}^{(1)}\right\}$$
$$- \frac{1}{2}\sum_{\nu'\nu''}C_{\nu'\nu''}^{RR}\left(\hat{K}_{3,\nu\nu'\nu''}^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\left\{\hat{K}_{3,\nu\nu'\nu''}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}\right\}\right). \tag{26}$$

The one-particle density matrix evolves according to

$$\frac{\partial\hat{\rho}_{\mathrm{e}}^{(1)}}{\partial t} = \frac{1}{\mathrm{i}\hbar}\left[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})},\hat{\rho}_{\mathrm{e}}^{(1)}\right] - \frac{1}{\mathrm{i}\hbar}\sum_{\nu}\left[\hat{F}_\nu^{(1)},\hat{\mu}_{1,\nu}^{(1)}\right]$$
$$+ \frac{1}{\mathrm{i}\hbar}\frac{1}{2}\sum_{\nu\nu'}C_{\nu\nu'}^{RR}\left[\hat{K}_{2,\nu\nu'}^{(1)},\hat{\rho}_{\mathrm{e}}^{(1)}\right] + \frac{1}{\mathrm{i}\hbar}\sum_{\nu\nu'}D_{\nu\nu'}^{RR}\left[\hat{J}_{\mu_{1,\nu}}^{(\mathrm{HF})},\hat{\mu}_{1,\nu'}^{(1)}\right] \tag{27}$$

and the correlation functions (moments) according to

$$\frac{\partial \hat{\mu}_{1,\nu}^{(1)}}{\partial t} = \frac{\hat{\lambda}_{1,\nu}^{(1)}}{M_\nu} + \frac{1}{i\hbar}\left[\hat{H}_e^{(HF)}, \hat{\mu}_{1,\nu}^{(1)}\right] + \frac{1}{i\hbar}\left[\hat{J}_{\mu_{1,\nu}}^{(HF)}, \hat{\rho}_e^{(1)}\right] - \frac{1}{i\hbar}\sum_{\nu'} C_{\nu\nu'}^{RR}\left[\hat{F}_{\nu'}^{(1)}, \hat{\rho}_e^{(1)}\right] \tag{28}$$

and

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

$$+ \tfrac{1}{2}\left(\hat{F}_\nu^{(1)}\hat{\rho}_e^{(1)} + \hat{\rho}_e^{(1)}\hat{F}_\nu^{(1)}\right) - \hat{\rho}_e^{(1)}\hat{F}_\nu^{(1)}\hat{\rho}_e^{(1)}$$

$$+ \sum_{\nu'\nu''} D_{\nu'\nu''}^{RR}\left(\mathrm{Tr}_{e,1}\left\{\hat{F}_\nu^{(1)}\hat{\mu}_{1,\nu'}^{(1)}\right\}\hat{\mu}_{1,\nu''}^{(1)} - \hat{\mu}_{1,\nu''}^{(1)}\hat{F}_\nu^{(1)}\hat{\mu}_{1,\nu'}^{(1)}\right)$$

$$- \sum_{\nu'}\left(\hat{K}_{2,\nu\nu'}^{(0)} + \mathrm{Tr}_{e,1}\left\{\hat{K}_{2,\nu\nu'}^{(1)}\hat{\rho}_e^{(1)}\right\}\right)\hat{\mu}_{1,\nu'}^{(1)}$$

$$- \tfrac{1}{2}\sum_{\nu'}\left(\hat{K}_{2,\nu\nu'}^{(1)}\hat{\mu}_{1,\nu'}^{(1)} + \hat{\mu}_{1,\nu'}^{(1)}\hat{K}_{2,\nu\nu'}^{(1)}\right)$$

$$+ \sum_{\nu'}\left(\hat{\mu}_{1,\nu'}^{(1)}\hat{K}_{2,\nu\nu'}^{(1)}\hat{\rho}_e^{(1)} + \hat{\rho}_e^{(1)}\hat{K}_{2,\nu\nu'}^{(1)}\hat{\mu}_{1,\nu'}^{(1)}\right)$$

$$- \tfrac{1}{4}\sum_{\nu'\nu''} C_{\nu'\nu''}^{RR}\left(\hat{K}_{3,\nu\nu'\nu''}^{(1)}\hat{\rho}_e^{(1)} + \hat{\rho}_e^{(1)}\hat{K}_{3,\nu\nu'\nu''}^{(1)} - 2\hat{\rho}_e^{(1)}\hat{K}_{3,\nu\nu'\nu''}^{(1)}\hat{\rho}_e^{(1)}\right) \tag{29}$$

with

$$J_{\lambda_{1,\nu}}^{(HF)}(1, 1') = \sum_{22'}\left(H_e^{(2)}(12, 1'2') - H_e^{(2)}(12, 2'1')\right)\lambda_{1,\nu}^{(1)}(2', 2). \tag{30}$$

3. Analysis of CEID

3.1. Trajectory interpretation

Having written down a set of 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 ion refers to the range of allowed trajectories available to it. Immediately we see that the average kinetic energy of an ion is determined not solely by the average momentum, but also by the spread of momentum

$$\bar{T}_I = \sum_\nu \frac{\overline{P_\nu^2}}{2M_\nu} = \sum_\nu \frac{1}{2M_\nu}\left(\bar{P}_\nu^2 + \overline{\Delta P_\nu^2}\right). \tag{31}$$

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

We begin with the simplest case, the Ehrenfest approximation. The ions 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 ionic trajectories there is similarly no dispersion of the electronic trajectories.

This latter point can be seen most clearly by examining the equation of motion for the density matrix in the Ehrenfest approximation:

$$i\hbar \frac{\partial \hat{\rho}_e}{\partial t} = \left[\hat{H}_e(\bar{R}), \hat{\rho}_e \right].$$

This equation has the property that the eigenvalues of $\hat{\rho}_e$ are constant in time. Thus, if the electronic system starts off in a pure state (a single many-electron state vector that could itself of course be a coherent mix of other state vectors), then it remains in a pure (though time evolving) state forever. 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 in a mean field sense.

Another way of phrasing this is that in the Ehrenfest approximation all *correlations* between electronic and ionic fluctuations have been suppressed. It is this feature that prevents it from properly describing the flow of energy from electrons to the ions [11]: the ions in the Ehrenfest approximation see, and interact with, an apparently structureless cold electron fluid (represented by the mean electron density) whose internal excitations remain hidden from the ions, and so heat flows predominantly from ions to electrons, leading to pathological ionic cooling even in situations where the reverse process should dominate. There can be a small flow the other way if the mean electron density becomes sufficiently rough, but this still provides quantitatively wrong results [9].

Thus we see that the correct energy transfer requires that the ions see the fluctuations in the electron gas, which by our earlier arguments means that the ions must also be allowed to fluctuate about their mean trajectory in a way that is correlated with the electron fluctuations.

Quantitative results can be obtained at the level of the first moment [8]. The explanation is as follows. Consider first the equation of motion for the electrons, dropping second-moment and higher terms

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

where we have unpacked $\hat{\mu}_{1,\nu}$. The first term is just the Ehrenfest term, so we focus on the second one. The quantity $\Delta \hat{R}_\nu \hat{F}_\nu$ 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: we are getting correlated fluctuations.

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

$$i\hbar \frac{\partial \hat{\rho}_e}{\partial t} = \left[\hat{H}_e, \hat{\rho}_e \right] + i\hbar \hat{\Gamma}. \tag{32}$$

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

$$\hat{\rho}_e = \sum_\alpha |\alpha(t)\rangle P_\alpha(t) \langle \alpha(t)|.$$

Then equation (32) gives

$$\frac{\partial P_\alpha(t)}{\partial t} = \langle \alpha(t)|\hat{\Gamma}|\alpha(t)\rangle.$$

Thus the eigenvalues of the many-electron density matrix can now change. This means that even if the electrons start off from a pure state, at later times they can in general no longer

be described by a pure state, but are described, rather, by an incoherent shower of states. Each member of this incoherent mix now corresponds to one out of an ensemble of possible evolutionary paths for the combined correlated electron–ion system.

So far we have not considered the *explicit* width of the ionic bundle of trajectories. This information is present in $\hat{\mu}_{1,\nu}$, but has to get there from somewhere, and that somewhere is the equation of motion which is given in equation (28). Information about the ionic width is provided explicitly by $C_{\nu\nu'}^{RR}$, while also propagating through from $\hat{\lambda}_{1,\nu}$ which depends on $C_{\nu\nu'}^{PR}$. Thus, by keeping electron–ion correlations up to the first moment ($\hat{\mu}_{1,\nu}$ and $\hat{\lambda}_{1,\nu}$) and ionic fluctuations up to the second moment we are able to capture essential features of the correlated electron–ion problem.

3.2. Connection with electron–phonon scattering 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 [11]

$$\hat{H}_0 = \hat{H}_e(R_0) - \sum_\nu \hat{F}_\nu(R_0)\hat{X}_\nu + \hat{T}_I + \tfrac{1}{2}\sum_{\nu\nu'} \hat{X}_\nu K_{\nu\nu'}^{\mathrm{BO}}\hat{X}_{\nu'} \tag{33}$$

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 [11]

$$\bar{H} = \hat{H}_e(\bar{R}) - \sum_\nu \hat{F}_\nu(\bar{R})\Delta\hat{R}_\nu + \hat{T}_I + \tfrac{1}{2}\sum_{\nu\nu'} \Delta\hat{R}_\nu K_{\nu\nu'}^{\mathrm{BO}}\Delta\hat{R}_{\nu'}. \tag{34}$$

For small variations in $\bar{R}$ about R_0, the two Hamiltonians 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 noninteracting 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

$$\dot{C}^{RR} = \frac{2}{M}C^{PR} \tag{35}$$

$$\dot{C}^{PR} = \frac{C^{PP}}{M} - K^{\mathrm{BO}}C^{RR} + \mathrm{Tr}_e\left\{\hat{F}\hat{\mu}\right\} \tag{36}$$

$$\dot{C}^{PP} = -2K^{\mathrm{BO}}C^{PR} + 2\,\mathrm{Tr}_e\left\{\hat{F}\hat{\lambda}\right\} \tag{37}$$

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

$$w = \frac{1}{M} \mathrm{Tr_e} \left\{ \hat{F}\hat{\lambda} \right\} \tag{38}$$

is the power dissipated into the ion by the electrons [11]. 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 equation (36). 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. Using the one-electron equations of motion given earlier we obtain

$$\dot{\hat{\rho}}_e = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\rho}_e] - \frac{1}{\mathrm{i}\hbar} [\hat{F}, \hat{\mu}] \tag{39}$$

$$\dot{\hat{\mu}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\mu}] - \frac{1}{\mathrm{i}\hbar} C^{RR} [\hat{F}, \hat{\rho}_e] + \frac{\hat{\lambda}}{M} \tag{40}$$

$$\dot{\hat{\lambda}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\lambda}] + \frac{1}{2} (\hat{F}\hat{\rho}_e + \hat{\rho}_e\hat{F}) - \hat{\rho}_e\hat{F}\hat{\rho}_e - \frac{1}{\mathrm{i}\hbar} C^{PR} [\hat{F}, \hat{\rho}_e] - K^{BO}\hat{\mu} \tag{41}$$

where we have discarded terms in $\hat{\mu}^2$ (in anticipation of a further approximation below). 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 realized by the quantity $\hat{F}$. To do a lowest order perturbative calculation we therefore now have to linearize the above equations in $\hat{F}$. Thus, we set $C^{PR} = 0$, $C^{RR} = C^{RR}(0) = n\hbar\omega/K^{BO}$, $n = N + 1/2$, $\omega^2 = K^{BO}/M$, and drop the last term in equation (39). 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 $\hat{z} = K^{BO}\hat{\mu}$ we get

$$\dot{z}_{\alpha\beta} = -\mathrm{i}\omega_{\alpha\beta}z_{\alpha\beta} + \omega^2\lambda_{\alpha\beta} + \mathrm{i}n\omega(f_\beta - f_\alpha)F_{\alpha\beta}$$

$$\dot{\lambda}_{\alpha\beta} = -\mathrm{i}\omega_{\alpha\beta}\lambda_{\alpha\beta} - z_{\alpha\beta} + \left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta \right) F_{\alpha\beta}$$

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 (38) 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)

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

$$+ \delta(\omega_{\beta\alpha} - \omega)[(N + 1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta] \}. \tag{42}$$

This expression is algebraically identical (after some rearrangement) to the corresponding result for the power dissipated into phonons by excited vibrations obtained by first-order scattering theory based on the standard electron–phonon Hamiltonian $\hat{H}_0$ given earlier [15].

We have demonstrated in a previous paper [8] 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 $z_{\alpha\beta} = K^{BO}\mu_{\alpha\beta}$ 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 (39) 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

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

This is algebraically identical to

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

The latter is the known quantum correlated electron–phonon scattering rate expression (from the Fermi Golden Rule), which incorporates the selection rules for inelastic current–voltage spectroscopy [16]. 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 [17]. We therefore assert, as will be shown by an explicit simulation later, 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 molecular dynamics that portrays these processes in real time.

4. Current-driven excitations and inelastic I–V spectroscopy in atomic wires

The method discussed in this paper is a technique for doing correlated electron–ion molecular dynamics, in order to describe the inelastic interactions between quantum electrons and quantum ions and the effect of these interactions and of the resultant energy exchange on the dynamics of the two subsystems. We illustrate the use of the method by a study of the interplay between inelastic electron–phonon interactions and transport in an atomic wire.

We have a 401-atom metallic atomic chain described by a tight binding model with all parameters as in [8] (these are the same as in [18] but with a different band filling). The middle
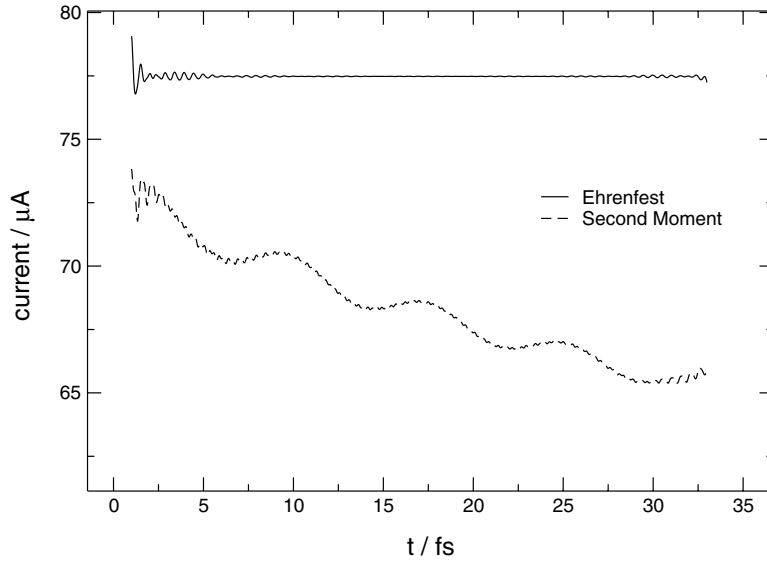
Figure 1. Current as a function of time after the application of a bias of 1 V in a metallic chain containing a single dynamical quantum ion, in the Ehrenfest approximation and in the second-moment expansion.

atom is allowed to move and is treated dynamically within the second-moment expansion. A bias is applied as follows. Initially, a static potential shift between the two halves of the chain is imposed; the electrons are placed in a state of equilibrium in the presence of the shift[6]; finally the external potential shift is relieved and current flows. We consider noninteracting electrons only (so all the $\hat{J}_q^{\text{HF}}$ matrices are zero). The use of this procedure to generate current flow in a finite system is a matter of convenience. We are developing an open boundary implementation of the method, already working at the levels of the Ehrenfest approximation [9] and the first-moment expansion of CEID [19], with an implementation of the second-moment expansion in the near future. Figure 1 shows the current as a function of time, following the application of a bias of 1 V. The dynamical ion starts off in the Born–Oppenheimer vibrational ground state[7]. In the Ehrenfest approximation the current is constant, while in the second-moment expansion it decreases in time. The reason for this decrease is the quantum heating of the ion as a result of inelastic electron–phonon scattering. This results in an increase in the scattering cross section, as measured by C^{RR}, that the ion presents to the electrons and a corresponding increase in resistance. As the figure shows, the Ehrenfest approximation remains oblivious to these inelastic effects. We furthermore showed in an earlier paper [8] that the first-moment expansion captures the quantum heating of the ion (via its quantum kinetic energy) but still fails to produce the feedback of the increasing ionic vibrational energy on the electrons and the current. The present results demonstrate that the second-moment expansion captures this feedback and the response of the resistance to the inelastic scattering.

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[6] In the present case, the initial electronic state was constructed with an effective electronic temperature $T_0^{\text{el}} = 500$ K. Since $k_B T_0^{\text{el}} = 0.043$ eV is much smaller than any of the relevant energy scales in the present simulations (set by the atomic masses and voltages considered below), we will ignore the finite value of T_0^{el} in the ensuing discussion.

[7] The initial ionic wavefunction enters the calculation via the initial conditions for the quantities C^{RR}, C^{PR}, C^{PP}. If we wish the ion, with mass M, to start off from a harmonic vibrational state with N phonons of frequency ω, then we write $C^{RR}(0) = (N + 1/2)\hbar/M\omega$, $C^{PR}(0) = 0$, $C^{PP}(0) = (N + 1/2)\hbar M\omega$. In figure 1 $N = 0$.
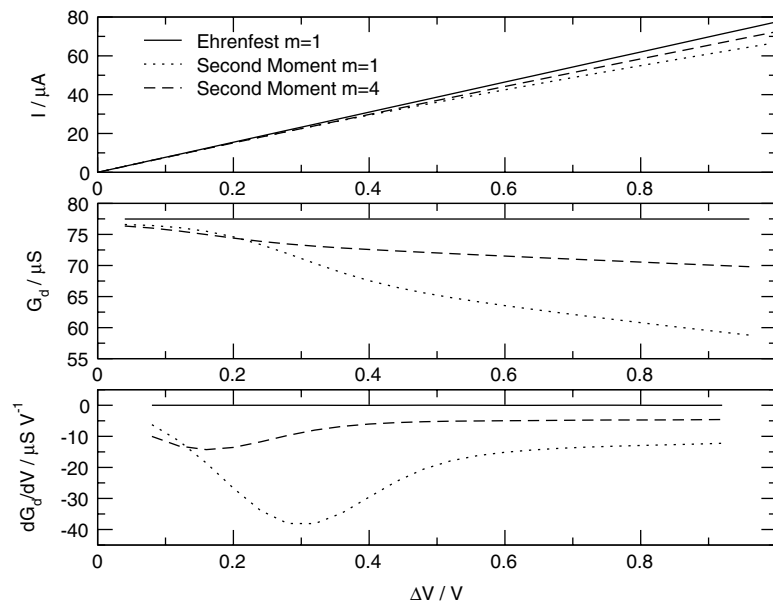
Figure 2. Current, differential conductance and its derivative with voltage, as a function of voltage, for a single dynamical atom in a metallic chain, for two values of the atomic mass.

This opens up the possibility of modelling inelastic current–voltage spectroscopy. The physical principle of this problem is the following. For current carrying electrons to be able to excite ionic 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.

Figure 2 shows the current, differential conductance and its derivative with voltage, as a function of voltage, for the above system, for two values of the mass of the dynamical ion: 1 amu and 4 amu. To make this plot, we have averaged the current for every voltage over a time equal to about one atomic vibration period following the application of the bias and the onset of current flow. The Ehrenfest approximation shows a ballistic linear current–voltage relation and is, once again, blind to the inelastic scattering in the system. The second-moment expansion, by contrast, clearly shows the characteristic inelastic spectral feature (in the bottom panel) due to the excitation of phonons by the current carrying electrons. 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.

According to lowest order electron–phonon scattering theory, with respect to a given reference Born–Oppenheimer surface, the inelastic spectral feature should occur at a voltage V that matches precisely the Born–Oppenheimer phonon frequency ω, on that same surface, $eV = \hbar\omega$ [16]. In the present case, for the lower of the two masses, $\hbar\omega = 0.26$ eV. We see that the results in the figure, obtained by second-moment CEID, agree well with this expectation.

To appreciate the significance of this agreement, let us consider how fundamentally different the two calculations actually are. One difference is that, by contrast with the scattering theory calculation, the full integrated second-moment equations of CEID are not perturbative and, in particular, they capture multiple successive electron–phonon interactions.

But there is a deeper (though related) difference. In the perturbative calculation, the effective phonon frequency, ω, that sets the energy exchanged in inelastic electron–ion interactions is introduced manually, by expanding the electron–ionic motion with respect to a particular (and fundamentally arbitrary) Born–Oppenheimer surface. Consider the effective Born–Oppenheimer stiffness matrix K^{BO}, from which the Born–Oppenheimer phonon frequencies are derived. It is given by

$$
\begin{aligned}
K_{\nu\nu'}^{\mathrm{BO}} &= \mathrm{Tr}_{\mathrm{e}}\left\{\hat{\rho}_{\mathrm{e}}^{\mathrm{BO}}\hat{H}_{\mathrm{e},\nu\nu'}\right\} + \mathrm{Tr}_{\mathrm{e}}\left\{\hat{\rho}_{\mathrm{e},\nu}^{\mathrm{BO}}\hat{H}_{\mathrm{e},\nu'}\right\} \\
&= \bar{K}_{\nu\nu'}^{\mathrm{BO}} + \Delta K_{\nu\nu'}^{\mathrm{BO}}
\end{aligned}
\tag{43}
$$

where subscript ν denotes differentiation with respect to that ionic degree of freedom, and the derivatives of the Born–Oppenheimer electron density matrix $\hat{\rho}_{\mathrm{e}}^{\mathrm{BO}}$ and $\hat{H}_{\mathrm{e}}$ are evaluated at the equilibrium classical ionic positions on the given reference Born–Oppenheimer surface. The first term in the above equation describes the stiffness that the ion would feel if the electron gas did not respond to ionic displacements. This bare stiffness, $\bar{K}^{\mathrm{BO}}$, is akin to the stiffness $\bar{K}_2$ appearing in our equations of motion. The correction ΔK^{BO}, on the other hand, takes account of the response of the electron gas to the ionic displacement. The bare stiffness $\bar{K}^{\mathrm{BO}}$ and the screened stiffness K^{BO} really are very different things, and in the present example $\bar{K}^{\mathrm{BO}} \sim 656\ \mathrm{J\ m^{-2}}$ while $K^{\mathrm{BO}} \sim 256\ \mathrm{J\ m^{-2}}$.

By contrast, SAME knows nothing about reference Born–Oppenheimer surfaces. Instead, it starts from scratch, with the bare electron–ion interaction. Indeed, the only stiffness that appears explicitly in the second-moment equations of motion is the unscreened stiffness $\bar{K}_2$, which corresponds to $\bar{K}^{\mathrm{BO}}$ above. SAME then faces the double task of first working its way through the electron–ion correlations needed to produce the relevant screening correction to the stiffness, playing the role of ΔK^{BO} above, and then generating the correlations, inelastic scattering and transitions beyond that. The fact that the inelastic current–voltage feature occurs at a voltage close to the expected value from scattering theory demonstrates that SAME really does accomplish this task. This in turn demonstrates that SAME is not a perturbative scheme but sums multiple correlated electron–ion interactions. We have found that the extended Hartree–Fock approximation for the two-electron density matrix, and the terms in the third line of equation (29) that it introduces, are essential for the theory to be able to capture correctly the screening of the electron–ion interaction by the electron gas.

A further agreement between the present simulations and scattering theory may be seen in the scaling of the voltage position and the height of the inelastic spectral feature with the mass of the dynamical ion (bottom plot of figure 2). According to the scattering calculation, both should scale as one over the square root of the atomic mass, and CEID broadly agrees with both expectations.

These crucial points of agreement aside, the results in figure 2 show some differences from lowest order scattering theory. In particular, the spectral feature is not *exactly* at the value that corresponds to the Born–Oppenheimer frequency, and the feature has acquired a finite width[8]. Regarding the first point, in view of the discussion above, there is in fact no reason to expect exact agreement. The fact that there *is* agreement, though not precise, is the remarkable thing.

Regarding the width of the feature, we can gain further insight as follows. We have repeated the calculation (for an atomic mass of 1 amu), for a longer chain (601 atoms), allowing longer times before multiple electron reflections off the chain ends begin to develop. In figure 3 we have calculated $\mathrm{d}G_d/\mathrm{d}V$ versus V by averaging the current for every voltage over a succession

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[8] In lowest order perturbation theory the spectral feature is a delta function, at most broadened by the ambient temperature T_0^{el} with which electrons approach the dynamical region. In the present case, once again, $T_0^{\mathrm{el}} = 500\ \mathrm{K}$ with $k_{\mathrm{B}}T_0^{\mathrm{el}} = 0.043\ \mathrm{eV}$.
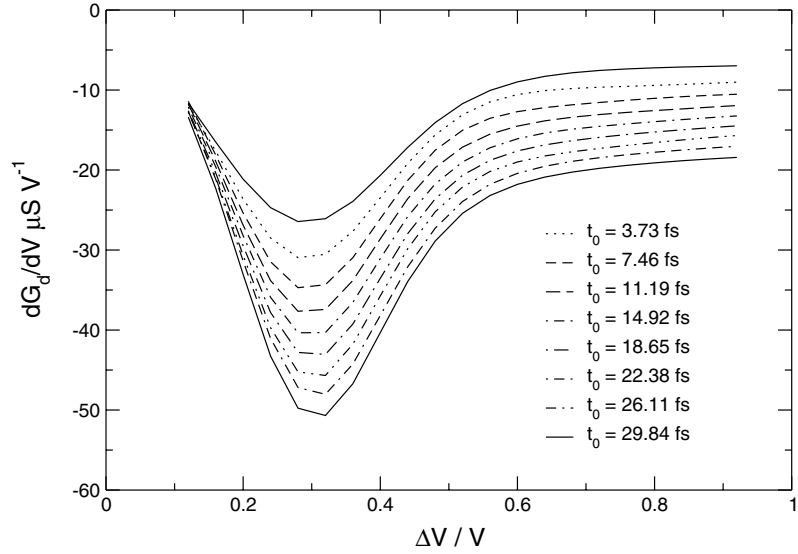
Figure 3. The second derivative of the current versus voltage, for a single dynamical atom in a metallic chain, calculated by averaging the current, for each voltage, over a series of time intervals, into the conduction process.

of time windows of fixed duration (about one atomic period as before), lying further and further into the conduction process. On the figure t_0 denotes the beginning of each time window, following the application of the bias. The vertical shift of the curve with increasing t_0 comes from the heating of the ion: once the bias exceeds the critical value at which electron–phonon scattering is activated, the ion picks up energy and its scattering cross section increases with time, so, for a given voltage, the longer we wait, the smaller the current (as we saw in figure 1). Of course, if we coupled our quantum ion to a heat bath, taking energy out of the ion, then this feature of the results would be modified, but that is not an issue we are interested in here. The scaling of the curve with t_0 involves also a slight shift in the horizontal position of the peak. However the width of the peak remains largely fixed. We therefore regard this width as an inherent feature of the system.

This width is due to the finite lifetimes and respective broadening of the electron and phonon spectra, due to the electron–ion interactions. We may, in particular, use the scattering rate expression from lowest order perturbation theory, given earlier, to estimate the lifetime of a phonon, τ_{ph}, against absorption by the electrons. For an Einstein oscillator of angular frequency ω and mass M in a ballistic metallic atomic chain, in the limit of zero electronic temperature (where, in the standard Landauer picture of the steady state, the occupancies for electrons approaching the dynamical atom from the two sides are step functions of energy, offset by the applied bias V), we get

$$\frac{1}{\tau_{\mathrm{ph}}} \sim \frac{2\pi}{M\omega} \frac{1}{\pi^2} \frac{H'^2}{H^2} \{[1 - \theta(|eV| - \hbar\omega)](\hbar\omega - |eV|) + \hbar\omega + |eV|\} \tag{44}$$

where θ is the step function, defined by $\theta(x) = 0$ for $x < 0$, $\theta(x) = 1$ otherwise, and H and H' are the tight binding nearest neighbour hopping integral and its derivative with distance. At $eV = \hbar\omega$ (the critical voltage where the inelastic current–voltage feature is expected to occur), with the present parameters, this gives $\tau_{\mathrm{ph}} \sim 48$ fs. This is comparable
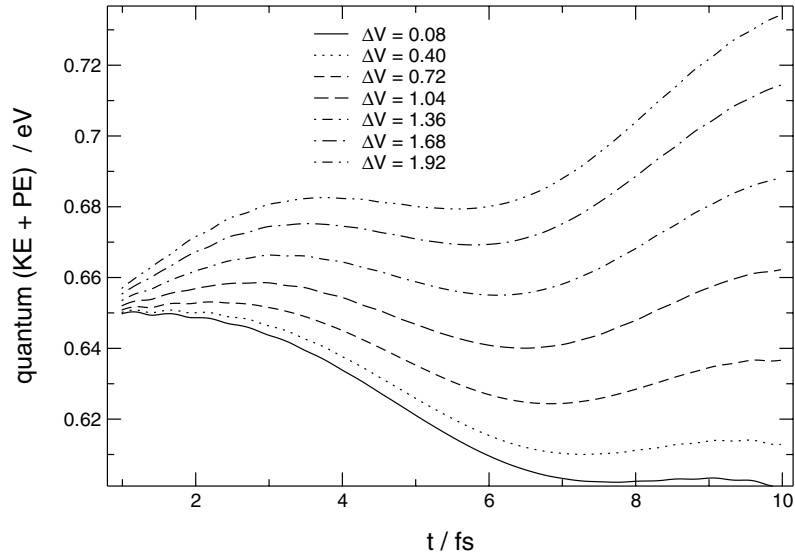
Figure 4. Ionic energy versus time as a function of voltage, for a fixed initial phonon energy.

with the Born–Oppenheimer period (16 fs), which is sufficient to broaden phonon energies, and corresponding spectral features, by amounts of the same order of magnitude as the actual energies. The fact that the simulations display this broadening demonstrates that CEID indeed allows electrons and phonons to perturb each other, in an internally consistent manner, through multiple successive interactions.

A central goal of the method is to enable energy exchange between electrons and ions both ways, depending on the relative degree of excitation of the two subsystems. To see this, in figure 4 we have plotted the ionic energy-like quantity $(C^{PP}/2M + K^{BO}C^{RR}/2)$ as a function of time. This quantity is the phonon energy that would be considered in the perturbative method. Due to the electron–ion correlations and multiple scattering, in CEID it is not possible to define unambiguously an ionic energy. However, for purposes of illustration we take the present quantity as a reasonable measure of such an energy. We consider an atomic mass of 1 amu and a series of voltages, for a fixed initial ionic energy (corresponding, numerically, to the second excited Born–Oppenheimer vibrational state, with $N = 2$ phonons). We see a crossover from ionic cooling at low V to ionic heating at high V. The voltage where the crossover occurs, as well as the effective prefactor, agree well with the analytical result, based on first-order scattering theory (equation (42) applied to the present system), for the power dissipated into the ion [11]:

$$w \approx \frac{2\pi\hbar}{M} \frac{1}{\pi^2} \frac{H'^2}{H^2} \left[-2U + (|eV| - \hbar\omega) \, \theta(|eV| - \hbar\omega) \right] \tag{45}$$

where $U = N\hbar\omega$ is the initial excess phonon energy, with $U = 2\hbar\omega$ in the present case. For this system, the Born–Oppenheimer value of $\hbar\omega$ is, once again, 0.26 eV. Thus, according to the formula the crossover from ionic cooling to heating should occur at $eV \sim 2U + \hbar\omega \sim 5\hbar\omega = 1.3$ eV, in broad agreement with the simulation. The prefactor in the formula is 0.01 fs^{-1}, in good agreement with the observed rate of heating of the ion, once the crossover occurs.

5. Conclusions

We have extended molecular dynamics to allow the electron and ion subsystems to feel and modify one another's fluctuations. This enables us to describe quantitatively the mutual excitations of the two subsystems, the energy exchanged in inelastic interactions and the effect of these interactions on the dynamics of the electrons and ions. By virtue of the fact that it is a form of molecular dynamics, the method portrays these processes in real time.

To accommodate simultaneously electron–electron and electron–ion correlations in our equations of motion, we have had to introduce a generalized Hartree–Fock approximation for the two-particle electron density matrix for an incoherent mix of electron states. This extended Hartree–Fock ansatz takes account of electron–ion correlations that are essential for bridging the gap between the bare electron–ion interaction and the true, screened interaction, in which the response of an ion to a passing electron is modified by the dynamics of the other electrons.

We have demonstrated that the SAME formalism reproduces the selection rules for electron–phonon scattering from perturbation theory. We have then employed the full second-moment equations of CEID to make dynamical simulations of mutually driven electron–ion excitations, inelastic current–voltage spectroscopy and energy dissipation in current carrying atomic wires. These simulations confirm the broad agreement between second-moment CEID and low order scattering theory, demonstrated analytically earlier, but show also significant differences. These differences bring out the following strengths of the present correlated electron–ion dynamical method:

  (i) it starts from scratch, bypassing the restrictive need to invoke reference Born–Oppenheimer surfaces, and Born–Oppenheimer phonons, in the description of electron–ion motion;

 (ii) it does not impose the assumption of harmonicity;

(iii) it is not perturbative.

To these we can add two further points. First, the method allows inelastic scattering and transitions to take place naturally, as is dictated by the quantum Liouville equation (i.e. the many-body time dependent electron–ion Schrödinger equation), without a need to impose *ad hoc* forms on these transitions, such as hops—instantaneous or not, random or not—between states. Second, the method includes the Pauli exclusion principle properly. Explicit equations for electron–electron interactions at the level of Hartree–Fock have been written down thereby introducing the mutual screening of the electron–electron and electron–ion interactions. Working out a practical computational scheme for this feature is work in progress.

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