Beyond Ehrenfest: correlated non-adiabatic molecular dynamics

2004 J. Phys.: Condens. Matter 16 8251

(http://iopscience.iop.org/0953-8984/16/46/012)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 8251–8266 PII: S0953-8984(04)84343-1

Beyond Ehrenfest: correlated non-adiabatic molecular dynamics

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

[1] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
[2] London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, UK
[3] School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, UK

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

Received 2 August 2004, in final form 11 October 2004
Published 5 November 2004
Online at stacks.iop.org/JPhysCM/16/8251
doi:10.1088/0953-8984/16/46/012

Abstract

A method for introducing correlations between electrons and ions that is computationally affordable is described. The central assumption is that the ionic wavefunctions are narrow, which makes possible a moment expansion for the full density matrix. To make the problem tractable we reduce the remaining many-electron problem to a single-electron problem by performing a trace over all electronic degrees of freedom except one. This introduces both one- and two-electron quantities into the equations of motion. Quantities depending on more than one electron are removed by making a Hartree–Fock approximation. Using the first-moment approximation, we perform a number of tight binding simulations of the effect of an electric current on a mobile atom. The classical contribution to the ionic kinetic energy exhibits cooling and is independent of the bias. The quantum contribution exhibits strong heating, with the heating rate proportional to the bias. However, increased scattering of electrons with increasing ionic kinetic energy is not observed. This effect requires the introduction of the second moment.

1. Introduction

A widely used description of systems of interacting electrons and ions is the Born–Oppenheimer, or adiabatic, approximation (BOA). The BOA is a scheme for decoupling the dynamics of the heavy and slow ions from the dynamics of the light and fast electrons. In the BOA one assumes that as ions move, the electronic subsystem remains in the thermodynamic state which minimizes its free energy, for the given instantaneous ionic positions.

Let us consider, in physical terms, two possible reasons for the failure of the BOA. First, if the ions move sufficiently fast, then the electronic subsystem will not have time to minimize its free energy before the ions undergo substantial further displacement. Put differently, the ionic motion, if it is sufficiently energetic, promotes excitations in the electron gas. The result is dissipation of energy by energetic ions into the electron gas. This mechanism for departures from the BOA is taken into account by Ehrenfest dynamics, at least in the limit of high ionic energies [1]. In Ehrenfest dynamics [2, 3] electrons and ions are allowed to evolve according to dynamical equations of motion, but, in these equations, the two sets of particles experience each other as external time-evolving classical mean fields. The ions are treated as classical particles, while the electrons are treated quantum mechanically.

There is a second, more subtle, mechanism for failure of the BOA which persists even in the limit of small ionic energy. Ions, however heavy by comparison with electrons, have a finite mass. Hence, as electrons jostle them, ions recoil, however slightly, and small amounts of energy are exchanged in these collisions. In other words, even classically, there is no such thing as an ionic position that remains unchanged throughout electronic equilibration, as is assumed in the BOA: ions constantly dance around in response to the electron gas as it attempts to find the state of thermodynamic equilibrium. The energy exchanged in these correlated electron–ion fluctuations causes the BOA to fail even in the limit of zero ionic temperature. This failure manifests itself as spontaneous phonon emission by excited electrons into the phonon vacuum [4, 5]. The correlation between electronic and ionic fluctuations, and the resultant dissipation of energy by excited electrons into cold vibrations, lies altogether beyond the scope of the Ehrenfest approximation.

In many problems it is possible to neglect these correlations. For example, the adiabatic approximation has been used extensively to model electronic conduction in nanoscale systems [6–12]. However, both the BOA and Ehrenfest dynamics are inadequate for describing Joule heating. This is a problem in which excited electrons dissipate energy into ionic vibrations, and for this problem the microscopic electron–ion correlations are *essential* [3, 13].

Despite the limitations just given, the Ehrenfest approximation has two virtues that we would like to retain:

(i) The classical description of the heavy ions provides an intuitive way to understand their motion and is readily handled using molecular dynamics.
(ii) The electrons can be treated accurately using a single-particle approach, such as time-dependent density functional theory.

Our task is to build on this foundation so as to introduce microscopic correlations as corrections to the dynamical equations. We achieve this by introducing a hierarchy of electron–ion correlation functions developed systematically as a moment expansion. We then make a Hartree–Fock approximation to the two-electron density matrix to allow the electrons to be treated within a single-particle picture that still respects their fermionic nature. Truncating the moment expansion after the first moment produces a closed and tractable set of equations that conserves total energy and takes account of electron–ion correlations. We apply the scheme to a current-carrying atomic wire and find that the ionic heating is recovered. However, the scheme lacks terms needed to accurately determine the reverse effect: the influence of ionic heating on the electronic current. The introduction of these terms from appropriate higher-order expansions is the subject of ongoing research.

This approach has a much wider range of applications than just heating of wires. In the first-moment approximation (treated explicitly below) this method could be applied to short timescale problems involving electron relaxation through phonon emission. This might include the early stages of the non-radiative decay of an excited electronic state in a molecule.

Once the second- (or higher-) moment approximation is made, the range of problems increases dramatically.

2. The small amplitude equations

In the Ehrenfest approximation the ions are treated as classical particles. Thus they are localized in space and their dynamics are completely characterized by their positions as a function of time. The Ehrenfest equations [14] (which are exact, but also give the name to the approximation) allow us to map the quantum expectation values of position ($\bar{R}_\nu$), momentum ($\bar{P}_\nu$) and force ($\bar{F}_\nu$) onto the corresponding classical quantities, yielding the following equations of motion:

$$\frac{\mathrm{d}\bar{R}_\nu}{\mathrm{d}t} = \frac{\bar{P}_\nu}{M_\nu}, \qquad \frac{\mathrm{d}\bar{P}_\nu}{\mathrm{d}t} = \bar{F}_\nu, \qquad \bar{F}_\nu = -\,\mathrm{Tr}\left\{\hat{\rho}\frac{\partial \hat{H}}{\partial \hat{R}_\nu}\right\}. \tag{1}$$

Here, $\hat{\rho}$, with $\mathrm{Tr}\{\hat{\rho}\} = 1$, is the full density matrix for the system of electrons and ions in the Schrödinger representation, $\hat{H}$ is its Hamiltonian, and $\bar{R}_\nu = \mathrm{Tr}\{\hat{\rho}\hat{R}_\nu\}$ and $\bar{P}_\nu = \mathrm{Tr}\{\hat{\rho}\hat{P}_\nu\}$, where $\hat{R}_\nu$ and $\hat{P}_\nu$ are the operators for a given ionic coordinate and the corresponding conjugate momentum, respectively. The index ν combines both the ion index and the component of its position (x, y, z). The mass of an ion is M_ν. The problem is to find $\hat{\rho}$. In general this is difficult, so instead we concentrate on evaluating certain expectation values that involve the density matrix. The equations of motion for these expectation values are considerably easier to work with numerically as the dimensionality of the matrices involved is greatly reduced compared to that of the full density matrix.

While classical mechanics may exaggerate the degree of localization of the ions, it is not completely wrong. We know that in many systems ions really are localized, as can be determined from x-ray diffraction or neutron scattering from crystals. Thus the average coordinate $\bar{R}_\nu$ is a physically meaningful quantity. This suggests that we might write the density matrix, using the spatial representation, as $\rho(\vec{r}_1 \ldots \vec{r}_n, \bar{R}_1 + \Delta R_1 \ldots \bar{R}_N + \Delta R_N; \vec{r}\,'_1 \ldots \vec{r}\,'_n, \bar{R}_1 + \Delta R'_1 \ldots \bar{R}_N + \Delta R'_N)$, where $\vec{r}_i$ is the position of an electron and ρ decays rapidly to zero as ΔR_ν increases from zero. Thus we only need consider the small amplitude fluctuations about the mean. This allows us to make the following Taylor expansion for the expectation value of the force on an ion (equation (1)):

$$\begin{aligned}
\bar{F}_\nu &= -\,\mathrm{Tr}\left\{\hat{\rho}\frac{\partial \hat{H}}{\partial \hat{R}_\nu}\right\} = -\,\mathrm{Tr}\left\{\hat{\rho}\left.\frac{\partial \hat{H}(\bar{R} + \Delta\hat{R})}{\partial \bar{R}_\nu}\right|_{\Delta\hat{R}}\right\} \\
&= -\,\mathrm{Tr}\left\{\hat{\rho}\left.\frac{\partial}{\partial \bar{R}_\nu}\right|_{\Delta\hat{R}}\left(\hat{H}(\bar{R}) + \sum_{\nu'}\frac{\partial \hat{H}(\bar{R})}{\partial \bar{R}_{\nu'}}\Delta\hat{R}_{\nu'} + \cdots\right)\right\} \\
&= \mathrm{Tr_e}\{\hat{\rho}_\mathrm{e}\hat{F}_\nu\} - \sum_{\nu'}\mathrm{Tr_e}\{\hat{\mu}_{\nu'}\hat{K}_{\nu'\nu}\} + \cdots
\end{aligned} \tag{2}$$

where $\Delta\hat{R}_\nu = \hat{R}_\nu - \bar{R}_\nu$, $\hat{R}$, $\bar{R}$ and $\Delta\hat{R}$ stand for the sets of values $\{\hat{R}_\nu\}$, $\{\bar{R}_\nu\}$ and $\{\Delta\hat{R}_\nu\}$ respectively, $\hat{F}_\nu = -\partial\hat{H}(\bar{R})/\partial\bar{R}_\nu$, $\hat{K}_{\nu\nu'} = \partial^2\hat{H}(\bar{R})/\partial\bar{R}_\nu\partial\bar{R}_{\nu'} = \hat{K}_{\nu'\nu}$, $\hat{\rho}_\mathrm{e} = \mathrm{Tr_I}\{\hat{\rho}\}$, $\hat{\mu}_\nu = \mathrm{Tr_I}\{\Delta\hat{R}_\nu\hat{\rho}\}$. By $\mathrm{Tr_e}\{\cdots\}$ and $\mathrm{Tr_I}\{\cdots\}$ we mean a trace over the electronic and ionic degrees of freedom respectively. Note that $\bar{R}_\nu$ is a number and not an operator, so $\hat{F}_\nu$ and $\hat{K}_{\nu\nu'}$ are purely *electronic* operators, as are $\hat{\rho}_\mathrm{e}$ and $\hat{\mu}_\nu$.

To evaluate the expectation value of the ionic force we need to determine the equations of motion of the electronic correlation functions $\hat{\rho}_\mathrm{e}$, $\hat{\mu}_\nu$ etc. In general one of these correlation functions can be represented by

$$\hat{q} = \mathrm{Tr_I}\{\hat{Q}(\Delta\hat{R}, \Delta\hat{P})\hat{\rho}\}, \tag{3}$$

where $\hat{q}$ is an electronic quantity, $\hat{Q}(\Delta\hat{R}, \Delta\hat{P})$ is a corresponding ionic quantity and $\Delta\hat{P}$ stands for the set of values $\{\Delta\hat{P}_\nu\}$ where $\Delta\hat{P}_\nu = \hat{P}_\nu - \bar{P}_\nu$. The equation of motion for $\hat{q}$ is

$$\begin{aligned}
\frac{\mathrm{d}\hat{q}}{\mathrm{d}t} &= \mathrm{Tr}_\mathrm{I}\left\{\sum_\nu\left(\frac{\bar{P}_\nu}{M_\nu}\frac{\partial\hat{Q}}{\partial\bar{R}_\nu} + \bar{F}_\nu\frac{\partial\hat{Q}}{\partial\bar{P}_\nu}\right)\hat{\rho}\right\} + \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_\mathrm{I}\{\hat{Q}[\hat{H}, \hat{\rho}]\} \\
&= \sum_\nu\frac{1}{2M_\nu}\mathrm{Tr}_\mathrm{I}\left\{\left(\Delta\hat{P}_\nu\frac{\partial\hat{Q}}{\partial\Delta\hat{R}_\nu} + \frac{\partial\hat{Q}}{\partial\Delta\hat{R}_\nu}\Delta\hat{P}_\nu\right)\hat{\rho}\right\} - \sum_\nu\bar{F}_\nu\,\mathrm{Tr}_\mathrm{I}\left\{\frac{\partial\hat{Q}}{\partial\Delta\hat{P}_\nu}\hat{\rho}\right\} \\
&\quad + \frac{1}{\mathrm{i}\hbar}[\hat{H}_\mathrm{e}(\bar{R}), \hat{q}] - \frac{1}{\mathrm{i}\hbar}\sum_\nu\left[\hat{F}_\nu, \mathrm{Tr}_\mathrm{I}\left\{\frac{1}{2}(\hat{Q}\Delta\hat{R}_\nu + \Delta\hat{R}_\nu\hat{Q})\hat{\rho}\right\}\right] \\
&\quad - \frac{1}{\mathrm{i}\hbar}\sum_\nu\frac{1}{2}(\hat{F}_\nu\,\mathrm{Tr}_\mathrm{I}\{[\hat{Q}, \Delta\hat{R}_\nu]\hat{\rho}\} + \mathrm{Tr}_\mathrm{I}\{[\hat{Q}, \Delta\hat{R}_\nu]\hat{\rho}\}\hat{F}_\nu) \\
&\quad + \frac{1}{\mathrm{i}\hbar}\frac{1}{2}\sum_{\nu\nu'}\left[\hat{K}_{\nu\nu'}, \mathrm{Tr}_\mathrm{I}\left\{\frac{1}{2}(\hat{Q}\Delta\hat{R}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}\hat{Q})\hat{\rho}\right\}\right] \\
&\quad + \frac{1}{\mathrm{i}\hbar}\frac{1}{2}\sum_{\nu\nu'}\frac{1}{2}(\hat{K}_{\nu\nu'}\,\mathrm{Tr}_\mathrm{I}\{[\hat{Q}, \Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}]\hat{\rho}\} + \mathrm{Tr}_\mathrm{I}\{[\hat{Q}, \Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}]\hat{\rho}\}\hat{K}_{\nu\nu'}) + \cdots
\end{aligned} \tag{4}$$

where $\hat{H} = \hat{T} + \hat{H}_\mathrm{e}$ and $\hat{T}$ is the total ionic kinetic energy operator, and we have made use of the Liouville equation $\mathrm{i}\hbar\partial\hat{\rho}/\partial t = [\hat{H}, \hat{\rho}]$ and the Ehrenfest equations (equation (1)). Equations (1), (2) and (4) constitute the *small amplitude equations*. Our purpose here is to use the moment expansion in equations (1), (2) and (4), where $\hat{q}$ is a general moment, to reinstate the correlation between light and heavy particles. The use of moment expansions to study quantum dynamics has a long history [15–18]. Recently it has been used to study the influence of quantum effects on the dynamics of atoms [19–22].

The equations that we have considered so far give us information about classical trajectories. However, we also need to know the evolution of the energy of the system, which depends on the spread of quantum trajectories about the classical one. In particular, the kinetic energy of the ions ($\bar{T}$) gives us a direct measure of the amount of heating that has taken place, while the total energy ($\bar{H}$) should be a conserved quantity. The total energy is indeed conserved, even for a truncated moment expansion, provided that the truncation is carried through in a systematic manner. By making a Taylor expansion for $\hat{H}_\mathrm{e}$ about the classical (mean) trajectory, we find that the rate of heating (w) is given by

$$\begin{aligned}
w = \frac{\mathrm{d}\bar{T}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}\{\hat{\rho}[\hat{T}, \hat{H}]\} \\
&= \sum_\nu\frac{1}{M_\nu}\left(\bar{P}_\nu\bar{F}_\nu + \mathrm{Tr}_\mathrm{e}\left\{\hat{F}_\nu\hat{\lambda}_\nu - \sum_{\nu'}\hat{K}_{\nu\nu'}\hat{\chi}_{\nu\nu'} + \cdots\right\}\right)
\end{aligned} \tag{5}$$

where $\hat{\lambda}_\nu = \mathrm{Tr}_\mathrm{I}\{\Delta\hat{P}_\nu\hat{\rho}\}$ and $\hat{\chi}_{\nu\nu'} = \frac{1}{2}\mathrm{Tr}_\mathrm{I}\{\hat{\rho}(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu)\}$.

3. Truncated expansions

To obtain a closed and tractable set of equations we need to truncate our series expansions after a finite number of moments. The moments that we need to consider involve powers of the ionic operators $\Delta\hat{R}_\nu$ and $\Delta\hat{P}_\nu$. We define the order of the moments as the sum of the powers of these operators. For example, first moments will involve $\Delta\hat{R}_\nu$ and $\Delta\hat{P}_\nu$, while second moments will involve $\Delta\hat{P}_\nu\Delta\hat{P}_{\nu'}$, $\Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}$, $\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'}$ and $\Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu$.

3.1. The zeroth-moment (Ehrenfest) approximation

In the zeroth-moment approximation the only correlation function that we retain is $\hat{\rho}_{\mathrm{e}}$ (the electronic density matrix). Therefore, from equations (2), (4) and (5) we get

$$\begin{aligned} \bar{F}_\nu &= \mathrm{Tr}_{\mathrm{e}}\{\hat{\rho}_{\mathrm{e}}\hat{F}_\nu\} \\ w &= \sum_\nu \frac{1}{M_\nu}\bar{P}_\nu\bar{F}_\nu \\ \frac{\mathrm{d}\hat{\rho}_{\mathrm{e}}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}(\bar{R}), \hat{\rho}_{\mathrm{e}}]. \end{aligned} \tag{6}$$

These equations correspond to the Ehrenfest approximation, and because of the absence of explicit correlation between electrons and ions they produce incorrect heating [3]. Therefore we have to go beyond this approximation.

3.2. The first-moment approximation

In the first-moment approximation the only correlation functions that we retain are $\hat{\rho}_{\mathrm{e}}$, $\hat{\mu}_\nu$ and $\hat{\lambda}_\nu$. From equations (2), (4) and (5) we get

$$\begin{aligned} \bar{F}_\nu &= \mathrm{Tr}_{\mathrm{e}}\{\hat{\rho}_{\mathrm{e}}\hat{F}_\nu\} - \sum_{\nu'}\mathrm{Tr}_{\mathrm{e}}\{\hat{\mu}_{\nu'}\hat{K}_{\nu'\nu}\} \\ w &= \sum_\nu \frac{1}{M_\nu}(\bar{P}_\nu\bar{F}_\nu + \mathrm{Tr}_{\mathrm{e}}\{\hat{F}_\nu\hat{\lambda}_\nu\}) \\ \frac{\mathrm{d}\hat{\rho}_{\mathrm{e}}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}(\bar{R}), \hat{\rho}_{\mathrm{e}}] - \frac{1}{\mathrm{i}\hbar}\sum_\nu[\hat{F}_\nu, \hat{\mu}_\nu] \\ \frac{\mathrm{d}\hat{\mu}_\nu}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}(\bar{R}), \hat{\mu}_\nu] + \frac{\hat{\lambda}_\nu}{M_\nu} \\ \frac{\mathrm{d}\hat{\lambda}_\nu}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}(\bar{R}), \hat{\lambda}_\nu] + \frac{1}{2}(\Delta\hat{F}_\nu\hat{\rho}_{\mathrm{e}} + \hat{\rho}_{\mathrm{e}}\Delta\hat{F}_\nu) - \frac{1}{2}\sum_{\nu'}(\hat{K}_{\nu\nu'}\hat{\mu}_{\nu'} + \hat{\mu}_{\nu'}\hat{K}_{\nu\nu'}) \end{aligned} \tag{7}$$

where $\Delta\hat{F}_\nu = \hat{F}_\nu - \bar{F}_\nu$. As a way of verifying the internal consistency of these equations we note the following. The three correlation functions each have a fixed trace: $\mathrm{Tr}_{\mathrm{e}}\{\hat{\rho}_{\mathrm{e}}\} = 1$, $\mathrm{Tr}_{\mathrm{e}}\{\hat{\mu}_\nu\} = 0$ and $\mathrm{Tr}_{\mathrm{e}}\{\hat{\lambda}_\nu\} = 0$. The equations of motion need to preserve these traces, which amounts to requiring that $\mathrm{Tr}_{\mathrm{e}}\{\mathrm{d}\hat{\rho}_{\mathrm{e}}/\mathrm{d}t\} = \mathrm{Tr}_{\mathrm{e}}\{\mathrm{d}\hat{\mu}_\nu/\mathrm{d}t\} = \mathrm{Tr}_{\mathrm{e}}\{\mathrm{d}\hat{\lambda}_\nu/\mathrm{d}t\} = 0$. It is straightforward to verify that these conditions are satisfied by equation (7). Further, if we define the first-moment approximation to the energy to be $E_1 = \bar{T} + \mathrm{Tr}_{\mathrm{e}}\{\hat{\rho}_{\mathrm{e}}\hat{H}_{\mathrm{e}}(\bar{R})\} - \sum_\nu \mathrm{Tr}_{\mathrm{e}}\{\hat{\mu}_\nu\hat{F}_\nu\}$, then we find that the first-moment approximation conserves energy. Here, $\bar{T}$ is found from

$$\bar{T} = \bar{T}_0 + \int_0^t w(s)\,\mathrm{d}s$$

with all quantities given by equation (7). The initial kinetic energy $\bar{T}_0$ is never evaluated.

Since $\bar{F}_\nu$ is a scalar and $\mathrm{Tr}_{\mathrm{e}}\{\hat{\lambda}_\nu\} = 0$, we may write the power w in equation (7) also as

$$w = \sum_\nu \frac{1}{M_\nu}(\bar{P}_\nu\bar{F}_\nu + \overline{\Delta F_\nu\Delta P_\nu}). \tag{8}$$

The first term in w, in which momentum and force are averaged separately, gives the rate of change of the classical ionic kinetic energy, $\sum_\nu \bar{P}_\nu^2/2M_\nu$. As we will see, this contribution to the power is akin to the power in Ehrenfest dynamics and gives predominantly ionic cooling. The second term in equation (8) gives, to first order, the rate of change of the quantum part of the ionic kinetic energy, $\sum_\nu \overline{\Delta P_\nu^2}/2M_\nu$. This term keeps track of the correlations between fluctuations in the force on an ion and in its momentum. We will see that this force–momentum correlation function gives the dissipation of energy from excited electrons into cold ions.

These equations introduce the correlations needed to produce heating in a current-carrying wire. As discussed in an earlier paper [3], what we require is correlation between the motion of individual electrons and individual ions. As observed in that paper this can be introduced by the correlation function $\hat{\mu}_\nu$. We can see this by considering the spatial representation of the diagonal elements of this electronic operator,

$$\mu_\nu(\vec{r}_1 \ldots \vec{r}_n; \vec{r}_1 \ldots \vec{r}_n) = \int \mathrm{d}R_1 \ldots \mathrm{d}R_N \, (R_\nu - \bar{R}_\nu) \\ \times \rho(\vec{r}_1 \ldots \vec{r}_n, R_1 \ldots R_N; \vec{r}_1 \ldots \vec{r}_n, R_1 \ldots R_N). \tag{9}$$

For a pure state these diagonal elements of the full density matrix just correspond to the modulus squared of the wavefunction. Therefore, we can interpret this correlation function as being the mean displacement of an ion from the average trajectory given that the electrons have positions given by $\vec{r}_1 \ldots \vec{r}_n$. That is, this correlation function has explicit information correlating the positions of individual ions with positions of individual electrons. Furthermore, we can see from these equations that the correlations introduce microscopic noise which is the source of heating. Fluctuations in the electron gas will produce microscopic fluctuations in the atomic forces through the term $-\sum_{\nu'} \mathrm{Tr}_\mathrm{e}\{\hat{\mu}_{\nu'} \hat{K}_{\nu'\nu}\}$, and quantum fluctuations in the atomic motion will similarly produce fluctuating forces on the electrons through the term $-\sum_\nu [\hat{F}_\nu, \hat{\mu}_\nu]/\mathrm{i}\hbar$. The fact that the fluctuations are transmitted between subsystems by the same correlation function is important because they are generated by collisions between particles within the subsystems: that is, one collision event simultaneously produces noise in both subsystems. The neglect of the second and higher moments can only be justified if the quantum fluctuations about the mean trajectory are small. As we shall see, higher moments are needed if the influence of ionic heating on the current is to be described accurately.

4. The Hartree–Fock approximation

All the equations given in the previous sections are for many-electron systems. These equations are computationally intractable in general because of the very large number of degrees of freedom that they represent. In standard Born–Oppenheimer calculations, this problem is often managed by transforming the exact many-particle equations into approximate mean field single-particle equations (the Hartree–Fock approximation). We take the same approach here. The first step is to define the electron–ion correlation functions for a single electron that correspond to the many-electron ones already given. This is achieved by carrying out traces over all the electrons except one:

$$\hat{\rho}_\mathrm{e}^{(1)} = N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{\rho}_\mathrm{e}\}, \qquad \hat{\mu}_\nu^{(1)} = N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{\mu}_\nu\}, \qquad \hat{\lambda}_\nu^{(1)} = N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{\lambda}_\nu\}. \tag{10}$$

Here $\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\cdots\}$ is an electronic trace over electrons $2, 3, 4, \ldots, N$. We have made use of the indistinguishability of electrons by making electron 1 representative of all the electrons.

Consider a pair of electron operators $\hat{a}^{(N)}$ and $\hat{b}^{(n)}$, where $\hat{a}^{(N)}$ depends on all N electronic degrees of freedom, while $\hat{b}^{(n)}$ depends upon $n \leqslant N$ electronic degrees of freedom. Now consider the one-electron operator $\hat{c}^{(1)}$ obtained by taking the trace over electrons $2 \ldots N$ of the product of the operators $\hat{a}^{(N)}$ and $\hat{b}^{(n)}$: $\hat{c}^{(1)} = N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{a}^{(N)}\hat{b}^{(n)}\}$.

There are two separate case to consider: when $\hat{b}^{(n)}$ depends on electron 1, and when it does not. For the former case we have (for $n \geqslant 1$)

$$\begin{aligned}\hat{c}^{(1)}(1) &= N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{a}^{(N)}(1\ldots N)\hat{b}^{(n)}(1\ldots n)\}\\ &= \frac{(N-n)!}{(N-1)!}\,\mathrm{Tr}_{\mathrm{e},2\ldots n}\{\hat{a}^{(n)}(1\ldots n)\hat{b}^{(n)}(1\ldots n)\}\end{aligned}\tag{11}$$

and for the latter case (for $n \geqslant 0$) we get

$$\begin{aligned}\hat{c}^{(1)}(1) &= N\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{\hat{a}^{(N)}(1\ldots N)\hat{b}^{(n)}(2\ldots n+1)\}\\ &= \frac{(N-n-1)!}{(N-1)!}\,\mathrm{Tr}_{\mathrm{e},2\ldots n+1}\{\hat{a}^{(n+1)}(1\ldots n+1)\hat{b}^{(n)}(2\ldots n+1)\}\\ &= \frac{(N-n-1)!}{(N-1)!}\,\mathrm{Tr}_{\mathrm{e},2\ldots n+1}\{\hat{b}^{(n)}(2\ldots n+1)\hat{a}^{(n+1)}(1\ldots n+1)\}\end{aligned}\tag{12}$$

where the n-electron operator $\hat{a}^{(n)}$ is given by $\hat{a}^{(n)} = (N!/(N-n)!)\,\mathrm{Tr}_{\mathrm{e},n+1\ldots N}\{\hat{a}^{(N)}\}$, and where we have made use of the fact that operators permute under a trace in the last line. The numerical arguments stand for the electrons on which the operators act, and are only used below when the equations would be ambiguous without them. Note that $\mathrm{Tr}_{\mathrm{e},2\ldots N}\{[\hat{a}^{(N)}, \hat{b}^{(n)}(2\ldots n+1)]\} = 0$, while in general $\mathrm{Tr}_{\mathrm{e},2\ldots N}\{[\hat{a}^{(N)}, \hat{b}^{(n)}(1\ldots n)]\} \neq 0$.

Both $\hat{F}_\nu$ and $\hat{K}_{\nu\nu'}$ are composed of a term that is independent of the electronic degrees of freedom (originating from the interaction between the ions) and a single-electron term (originating from the interaction between the electrons and the ions). Therefore, these operators can be written as $\hat{F}_\nu = \hat{F}_\nu^{(0)} + \sum_i \hat{F}_\nu^{(1)}(i)$ and $\hat{K}_{\nu\nu'} = \hat{K}_{\nu\nu'}^{(0)} + \sum_i \hat{K}_{\nu\nu'}^{(1)}(i)$, where i is an index running over all the electrons[4]. The Hamiltonian operator $\hat{H}_\mathrm{e}$ also has zero- and one-electron terms (the ion–ion interaction, $\hat{H}_\mathrm{e}^{(0)}$, and the electronic kinetic energy plus the electron–ion interaction, $\sum_i \hat{H}_\mathrm{e}^{(1)}(i)$). However, it also has a two-electron term (the electron–electron term, $\frac{1}{2}\sum_{ij}\hat{H}_\mathrm{e}^{(2)}(ij)$).

4.1. The zeroth-moment (Ehrenfest) approximation

Consider the equation of motion for the one-particle electron density matrix in the Ehrenfest (zeroth-moment) approximation (equation (6)):

$$\begin{aligned}\frac{\mathrm{d}\hat{\rho}_\mathrm{e}^{(1)}(1)}{\mathrm{d}t} &= \frac{N}{\mathrm{i}\hbar}\,\mathrm{Tr}_{\mathrm{e},2\ldots N}\{[\hat{H}_\mathrm{e}, \hat{\rho}_\mathrm{e}(123\ldots N)]\}\\ &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_\mathrm{e}^{(1)}(1), \hat{\rho}_\mathrm{e}^{(1)}(1)] + \frac{1}{\mathrm{i}\hbar}\,\mathrm{Tr}_{\mathrm{e},2}\{[\hat{H}_\mathrm{e}^{(2)}(12), \hat{\rho}_\mathrm{e}^{(2)}(12)]\}.\end{aligned}\tag{13}$$

We now make the Hartree–Fock approximation for the two-particle density matrix [23]. This requires some additional notation. We define the elements of the single-particle density matrix $\rho_\mathrm{e}^{(1)}(1; 1')$ by $\rho_\mathrm{e}^{(1)}(1; 1') = \langle 1|\hat{\rho}_\mathrm{e}^{(1)}|1'\rangle$, where the set of states $\{|1\rangle\}$ spans the space available to electron 1. Similarly, for the two-particle matrix we have $\rho_\mathrm{e}^{(2)}(12; 1'2') = \langle 12|\hat{\rho}_\mathrm{e}^{(1)}|1'2'\rangle$. The Hartree–Fock approximation is $\rho_\mathrm{e}^{(2,\mathrm{HF})}(12; 1'2') = \rho_\mathrm{e}^{(1)}(1; 1')\rho_\mathrm{e}^{(1)}(2; 2') - \rho_\mathrm{e}^{(1)}(1; 2')\rho_\mathrm{e}^{(1)}(2; 1')$, which allows us to write equation (13) as

$$\frac{\mathrm{d}\hat{\rho}_\mathrm{e}^{(1)}}{\mathrm{d}t} = \frac{1}{\mathrm{i}\hbar}[\hat{H}_\mathrm{e}^{(\mathrm{HF})}, \hat{\rho}_\mathrm{e}^{(1)}],\tag{14}$$

where the single-particle Hamiltonian $\hat{H}_\mathrm{e}^{(\mathrm{HF})}$ is the Fock operator whose matrix representation is

$$H_\mathrm{e}^{(\mathrm{HF})}(1; 1') = H_\mathrm{e}^{(1)}(1; 1') + \sum_{22'}(H_\mathrm{e}^{(2)}(12; 1'2') - H_\mathrm{e}^{(2)}(12; 2'1'))\rho_\mathrm{e}^{(1)}(2'; 2).\tag{15}$$

---

[4] A quantity such as $\hat{K}_{\nu\nu'}^{(0)}$ that does not depend on the electronic degrees of freedom may also be viewed as a scalar, call it $K_{\nu\nu'}$, multiplied by the identity operator in the N-electron Hilbert space: $\hat{K}_{\nu\nu'}^{(0)} = K_{\nu\nu'}\sum_{i=1}^{N}\hat{1}_\mathrm{e}(i)/N$, where $\hat{1}_\mathrm{e}(i)$ is the one-electron unit operator for electron i.

Note that these equations require the single-electron density matrix to be idempotent:

$$\hat{\rho}_{\mathrm{e}}^{(1)} = \hat{\rho}_{\mathrm{e}}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}. \tag{16}$$

The atomic force is given by $\bar{F}_{\nu} = \hat{F}_{\nu}^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\{\hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}\}$. These equations correspond very closely to ones derived in earlier work based on a density functional theory description of the electrons [2].

4.2. The first-moment approximation

If we repeat the procedure used above (using traces to eliminate all but one particle, and making the Hartree–Fock approximation for the two-particle density matrix) we obtain the following equations for the first-moment approximation:

$$\begin{aligned}
\bar{F}_{\nu} &= \hat{F}_{\nu}^{(0)} + \mathrm{Tr}_{\mathrm{e},1}\{\hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}\} - \sum_{\nu'}\mathrm{Tr}_{\mathrm{e},1}\{\hat{\mu}_{\nu'}^{(1)}\hat{K}_{\nu'\nu}^{(1)}\} \\
w &= \sum_{\nu}\frac{1}{M_{\nu}}(\bar{P}_{\nu}\bar{F}_{\nu} + \mathrm{Tr}_{\mathrm{e},1}\{\hat{F}_{\nu}^{(1)}\hat{\lambda}_{\nu}^{(1)}\}) \\
\frac{\mathrm{d}\hat{\rho}_{\mathrm{e}}^{(1)}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}, \hat{\rho}_{\mathrm{e}}^{(1)}] - \frac{1}{\mathrm{i}\hbar}\sum_{\nu}[\hat{F}_{\nu}^{(1)}, \hat{\mu}_{\nu}^{(1)}] \\
\frac{\mathrm{d}\hat{\mu}_{\nu}^{(1)}(1)}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(1)}(1), \hat{\mu}_{\nu}^{(1)}(1)] + \mathrm{Tr}_{\mathrm{e},2}\left\{\frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(2)}(12), \hat{\mu}_{\nu}^{(2)}(12)]\right\} + \frac{\hat{\lambda}_{\nu}^{(1)}(1)}{M_{\nu}} \\
\frac{\mathrm{d}\hat{\lambda}_{\nu}^{(1)}(1)}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(1)}(1), \hat{\lambda}_{\nu}^{(1)}(1)] + \mathrm{Tr}_{\mathrm{e},2}\left\{\frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(2)}(12), \hat{\lambda}_{\nu}^{(2)}(12)]\right\} \\
&\quad + \tfrac{1}{2}(\hat{F}_{\nu}^{(1)}(1)\hat{\rho}_{\mathrm{e}}^{(1)}(1) + \hat{\rho}_{\mathrm{e}}^{(1)}(1)\hat{F}_{\nu}^{(1)}(1)) \\
&\quad - \hat{\rho}_{\mathrm{e}}^{(1)}(1)\hat{F}_{\nu}^{(1)}(1)\hat{\rho}_{\mathrm{e}}^{(1)}(1) \\
&\quad + \sum_{\nu'}\mathrm{Tr}_{\mathrm{e},1}\{\hat{\mu}_{\nu'}^{(1)}(1)\hat{K}_{\nu'\nu}^{(1)}(1)\}\hat{\rho}_{\mathrm{e}}^{(1)}(1) - \sum_{\nu'}\hat{K}_{\nu\nu'}^{(0)}\hat{\mu}_{\nu'}^{(1)}(1) \\
&\quad - \tfrac{1}{2}\sum_{\nu'}(\hat{K}_{\nu\nu'}^{(1)}(1)\hat{\mu}_{\nu'}^{(1)}(1) + \hat{\mu}_{\nu'}^{(1)}(1)\hat{K}_{\nu\nu'}^{(1)}(1)) \\
&\quad - \sum_{\nu'}\mathrm{Tr}_{\mathrm{e},2}\{\hat{\mu}_{\nu'}^{(2)}(12)\hat{K}_{\nu'\nu}^{(1)}(2)\}
\end{aligned} \tag{17}$$

where $\hat{\mu}_{\nu}^{(2)} = N(N-1)\,\mathrm{Tr}_{\mathrm{e},3\ldots N}\{\hat{\mu}_{\nu}\}$ and $\hat{\lambda}_{\nu}^{(2)} = N(N-1)\,\mathrm{Tr}_{\mathrm{e},3\ldots N}\{\hat{\lambda}_{\nu}\}$. We now make a Hartree–Fock approximation for the two-electron correlation functions (see the appendix for the proof). From equation (A.5) we get

$$\begin{aligned}
\mu_{\nu}^{(2,\mathrm{HF})}(12, 1'2') &= \mu_{\nu}^{(1)}(1, 1')\rho_{\mathrm{e}}^{(1)}(2, 2') + \rho_{\mathrm{e}}^{(1)}(1, 1')\mu_{\nu}^{(1)}(2, 2') \\
&\quad - \mu_{\nu}^{(1)}(1, 2')\rho_{\mathrm{e}}^{(1)}(2, 1') - \rho_{\mathrm{e}}^{(1)}(1, 2')\mu_{\nu}^{(1)}(2, 1') \\
\lambda_{\nu}^{(2,\mathrm{HF})}(12, 1'2') &= \lambda_{\nu}^{(1)}(1, 1')\rho_{\mathrm{e}}^{(1)}(2, 2') + \rho_{\mathrm{e}}^{(1)}(1, 1')\lambda_{\nu}^{(1)}(2, 2') \\
&\quad - \lambda_{\nu}^{(1)}(1, 2')\rho_{\mathrm{e}}^{(1)}(2, 1') - \rho_{\mathrm{e}}^{(1)}(1, 2')\lambda_{\nu}^{(1)}(2, 1')
\end{aligned} \tag{18}$$

with the corresponding idempotency conditions

$$\begin{aligned}
\hat{\mu}_{\nu}^{(1)} &= \hat{\rho}_{\mathrm{e}}^{(1)}\hat{\mu}_{\nu}^{(1)} + \hat{\mu}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} \\
\hat{\lambda}_{\nu}^{(1)} &= \hat{\rho}_{\mathrm{e}}^{(1)}\hat{\lambda}_{\nu}^{(1)} + \hat{\lambda}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}.
\end{aligned} \tag{19}$$

To see what this means, let $\hat{\rho}_{\mathrm{e}}^{(1)} = \sum_{\alpha}|\alpha\rangle f_{\alpha}\langle\alpha|$ and $\langle\alpha|\hat{\mu}_{\nu}^{(1)}|\alpha'\rangle = \mu_{\nu,\alpha\alpha'}$. Then we have

$$\mu_{\nu,\alpha\alpha'} = (f_{\alpha} + f_{\alpha'})\mu_{\nu,\alpha\alpha'} \Rightarrow 0 = (f_{\alpha} + f_{\alpha'} - 1)\mu_{\nu,\alpha\alpha'}. \tag{20}$$

Thus $\mu_{\nu,\alpha\alpha'} = 0$ unless $f_{\alpha} + f_{\alpha'} - 1 = 0$. For an idempotent density matrix, $f_{\alpha} \in \{0, 1\}$; thus $\mu_{\nu,\alpha\alpha'}$ is zero in the occupied and empty blocks, but non-zero in the off-diagonal blocks coupling occupied and empty states. That is, its effect in the equation of motion for $\hat{\rho}_{\mathrm{e}}^{(1)}$ (see equation (17)) is to transfer electrons from occupied to empty states.

Substituting equations (18) and (19) into equation (17) we get

$$\begin{aligned}
\frac{\mathrm{d}\hat{\mu}_{\nu}^{(1)}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}, \hat{\mu}_{\nu}^{(1)}] + \frac{1}{\mathrm{i}\hbar}[\hat{I}_{\nu}^{(\mathrm{HF})}, \hat{\rho}_{\mathrm{e}}^{(1)}] + \frac{\hat{\lambda}_{\nu}^{(1)}}{M_{\nu}} \\
\frac{\mathrm{d}\hat{\lambda}_{\nu}^{(1)}}{\mathrm{d}t} &= \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}, \hat{\lambda}_{\nu}^{(1)}] + \frac{1}{\mathrm{i}\hbar}[\hat{J}_{\nu}^{(\mathrm{HF})}, \hat{\rho}_{\mathrm{e}}^{(1)}] - \sum_{\nu'} \bar{K}_{\nu\nu'}\hat{\mu}_{\nu'}^{(1)} \\
&\quad - \hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} + \tfrac{1}{2}(\hat{F}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} + \hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}) \\
&\quad + \sum_{\nu'}(\hat{\mu}_{\nu'}^{(1)}\hat{K}_{\nu\nu'}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} + \hat{\rho}_{\mathrm{e}}^{(1)}\hat{K}_{\nu\nu'}^{(1)}\hat{\mu}_{\nu'}^{(1)}) - \tfrac{1}{2}\sum_{\nu'}(\hat{K}_{\nu\nu'}^{(1)}\hat{\mu}_{\nu'}^{(1)} + \hat{\mu}_{\nu'}^{(1)}\hat{K}_{\nu\nu'}^{(1)}).
\end{aligned} \tag{21}$$

The terms in the last two lines above keep track of the fermionic statistics of the electrons. Note that the traces of all the equations of motion are zero provided that the idempotency conditions apply. The new Hartree–Fock operators $\hat{I}_{\nu}^{(\mathrm{HF})}$ and $\hat{J}_{\nu}^{(\mathrm{HF})}$ are given by equations (A.10) and (A.12).

To gain further insight into these equations consider the limit $M_{\nu} \to \infty$. We neglect the operators $\hat{I}_{\nu}^{(\mathrm{HF})}$ and $\hat{J}_{\nu}^{(\mathrm{HF})}$. In the limit of heavy ions, from equation (21) we get $\mathrm{d}\hat{\mu}_{\nu}^{(1)}/\mathrm{d}t \approx [\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}(\bar{R}), \hat{\mu}_{\nu}^{(1)}]/\mathrm{i}\hbar$. If $\hat{\mu}_{\nu}^{(1)}(0) = 0$, then $\hat{\mu}_{\nu}^{(1)} = 0$ for all time. In this case the equations split into two uncoupled sets: the Ehrenfest approximation plus

$$\frac{\mathrm{d}\hat{\lambda}_{\nu}^{(1)}}{\mathrm{d}t} \approx \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}(\bar{R}), \hat{\lambda}_{\nu}^{(1)}] + \frac{1}{2}(\hat{F}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)} + \hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}) - \hat{\rho}_{\mathrm{e}}^{(1)}\hat{F}_{\nu}^{(1)}\hat{\rho}_{\mathrm{e}}^{(1)}. \tag{22}$$

For a steady current, the electron density matrix will commute with the Hamiltonian, and therefore the density matrix and Hamiltonian will share eigenvectors. If the Hamiltonian and the density matrix satisfy the equations $\hat{H}_{\mathrm{e}}^{(\mathrm{HF})}|\alpha\rangle = \epsilon_{\alpha}|\alpha\rangle$ and $\hat{\rho}_{\mathrm{e}}^{(1)}|\alpha\rangle = f_{\alpha}|\alpha\rangle$ respectively, then we can express equation (22) as

$$\frac{\mathrm{d}\lambda_{\nu,\alpha\beta}^{(1)}}{\mathrm{d}t} \approx \frac{\epsilon_{\alpha} - \epsilon_{\beta}}{\mathrm{i}\hbar}\lambda_{\nu,\alpha\beta}^{(1)} + \frac{f_{\alpha}(1 - f_{\beta}) + f_{\beta}(1 - f_{\alpha})}{2}F_{\nu,\alpha\beta}^{(1)}$$

where $\lambda_{\nu,\alpha\beta}^{(1)} = \langle\alpha|\hat{\lambda}_{\nu}^{(1)}|\beta\rangle$ and $F_{\nu,\alpha\beta}^{(1)} = \langle\alpha|\hat{F}_{\nu}^{(1)}|\beta\rangle$. The solution is

$$\lambda_{\nu,\alpha\beta}^{(1)}(t) = \frac{f_{\alpha}(1 - f_{\beta}) + f_{\beta}(1 - f_{\alpha})}{2}F_{\nu,\alpha\beta}^{(1)}\frac{(1 - \mathrm{e}^{-\mathrm{i}\omega_{\alpha\beta}t})}{\mathrm{i}\omega_{\alpha\beta}}$$

where $\hbar\omega_{\alpha\beta} = \epsilon_{\alpha} - \epsilon_{\beta}$. In the limit $t \to \infty$, $\sin\omega_{\alpha\beta}t/\omega_{\alpha\beta} \to \pi\delta(\omega_{\alpha\beta})$. Substituting in equation (17), for the power w we find $w \to \sum_{\nu}(\bar{P}_{\nu}\bar{F}_{\nu} + 2\pi\hbar\sum_{\alpha\beta}|F_{\nu,\alpha\beta}^{(1)}|^2 f_{\alpha}(1 - f_{\beta})\delta(\epsilon_{\alpha} - \epsilon_{\beta}))/M_{\nu}$, where a factor of 2 for spin degeneracy has been included. The significance of this expression is that the second term agrees with the heating term from quantum perturbation theory, in the limit of large bias [24].

5. Simulations

To test the ability of these equations to reproduce current-induced heating in a wire, we have performed a series of simulations using the program DINAMO. We have looked at the rate of heating (increase in ionic kinetic energy) as a function of the applied bias. The model system that we have considered consists of 701 atoms in a chain. The electronic structure of the system is modelled using the time-dependent orthogonal tight binding approach [1], with a single s orbital and one electron per atom. (We actually used 702 electrons; an even number is

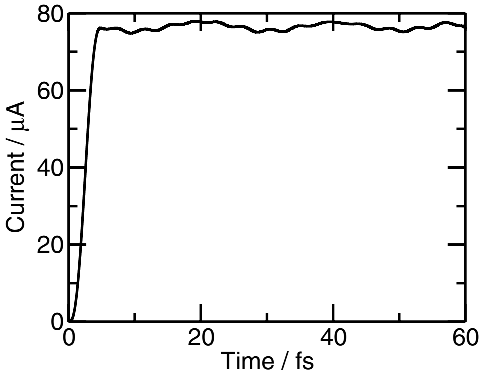

Figure 1. The current through the wire as a function of time for an applied bias of 1 V. Note that the time-dependent formalism produces a steady current.

necessary to ensure that we have an idempotent density matrix.) This is a single-particle model so we have no contribution from the operators $\hat{I}_{\nu}^{(\mathrm{HF})}$ and $\hat{J}_{\nu}^{(\mathrm{HF})}$. The rest of the parameters of the model are taken from [25]. The positions of all the atoms are held fixed, with the exception of that of the middle atom in the chain which is allowed to move in one dimension. It has a mass of $1/30$ the atomic mass of gold (about 6.6 atomic mass units). In the present simulations, electrons are treated as non-interacting.

A current is induced (and the bias is defined) by the following scheme [2, 3, 26]. At the start of the simulation we move electrons from one side of the wire to the other, creating an excess of electrons on one side (let us say, the left-hand side) and a deficit on the other side (the right-hand side). We accomplish this in two steps. First we apply a uniform external potential to the left-hand side of the wire, and find the electronic ground state of the entire system; the size of the applied external potential defines the magnitude of the bias. In the next step the external potential is turned off smoothly over a short time. This causes the excess of electrons on the left-hand side to begin to move over to the right-hand side, producing an electric current[5]. A steady current continues to flow until there is no longer an electron excess on one side, after which the electrons continue to evolve in time, oscillating backwards and forwards between the two sides of the wire. However, the only section of the dynamics in which we are interested is the initial part, before the current first changes direction.

During the simulation we integrate equations (1), (17) and (21) forward in time. The velocity Verlet algorithm is used for the classical degrees of freedom ($\bar{R}$ and $\bar{P}$), while the following simple integrator is used for the electronic case: $f(t + \Delta t) = f(t - \Delta t) + 2\Delta t f'(t)$ [27]. A time step size of 8×10^{-18} s was used. The conservation of total energy is found to be very good, the maximum error being between 10^{-7} and 10^{-8} eV. This procedure is furthermore unitary, in the sense that it identically preserves the trace of the density matrix. In figure 1 is shown the current passing through the wire as a function of time. Once the external potential has been reduced to zero, the current becomes steady with small amplitude, high-frequency oscillations whose frequency is determined by the bias, and lower-frequency oscillations as a result of the motion of the mean atomic coordinate.

The main purpose of these simulations is to investigate the heating of the mobile atom produced by the current. This heating is measured through the total kinetic energy of the mobile

---

[5] We may view the initial situation as one in which the two halves of our system are made of two different metals. Our initial density matrix is thus the ground state density matrix for this bimetallic junction, with a higher electron density on one side (the left-hand side in the present case) than on the other. Lifting the applied bias is then equivalent to making the two metals the same.

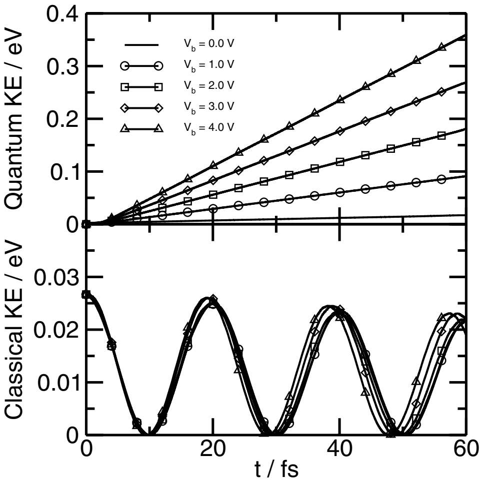

Figure 2. The classical and quantum contributions to the ionic kinetic energy as a function of time for a range of applied biases. Note the difference by a factor of 10 between the energy scales for classical and quantum contributions.

atom: the kinetic energy increases when the ion heats up, and decreases when the ion cools down. As was observed earlier, there are two components to the ionic kinetic energy, namely the classical component ($T_\nu^{(c)} = \bar{P}_\nu^2/2M_\nu$) and the quantum component ($T_\nu^{(q)} = \mathrm{Tr}\{\hat{\rho}\Delta\hat{P}_\nu^2\}/2M_\nu$). In practice we evaluate the *change* in the quantum component of the kinetic energy by integrating the quantum component of the power, $\Delta T_\nu^{(q)}(t) = \int_0^t \mathrm{Tr}_\mathrm{e}\{\hat{F}_\nu(s)\hat{\lambda}_\nu(s)\}\mathrm{d}s/M_\nu$. The two contributions to the kinetic energy for the mobile atom, as a function of the bias, are shown in figure 2.

There are five important features to note.

(i) First, the energy scale for the quantum kinetic energy is ten times that of the classical kinetic energy. That is, once heating begins the quantum contribution swiftly dominates.
(ii) Second, the classical contribution oscillates in time following the motion of the average position of the mobile atom. In contrast the quantum contribution grows linearly in time, with the slope (quantum power, $w^{(q)}$) varying linearly with the bias; we find $\Delta w^{(q)}/\Delta V_\mathrm{bias} \approx 0.26\ \mu\mathrm{A}$, consistent with the quantum perturbation result [24].
(iii) Third, the quantum contribution increases as time increases, while the maximum of the classical contribution decreases as time increases. The conservation of energy is mostly achieved by a corresponding net decrease in the terms $\mathrm{Tr}_{\mathrm{e},1}\{\hat{\rho}_\mathrm{e}^{(1)}\hat{H}_\mathrm{e}^{(\mathrm{HF})}\} + \hat{H}^{(0)}$. There is very little change to the term $\sum_\nu \mathrm{Tr}_{\mathrm{e},1}\{\hat{\mu}_\nu^{(1)}\hat{F}_\nu^{(1)}\}$.
(iv) Fourth, the rate of increase of the quantum contribution grows linearly with the applied bias, whereas the rate of decrease of the classical contribution is almost independent of bias.
(v) Finally, there is an increase in frequency of oscillation of the classical kinetic energy with increasing bias. This is a consequence of the population of anti-bonding states as the bias is increased, and would be observed in a Born–Oppenheimer calculation as well.

As observed in our earlier work [3], there are both heating and cooling processes taking place. The cooling processes are apparent in the classical kinetic energy (which is consistent with the strong tendency towards cooling in the Ehrenfest approximation [3]), while the heating

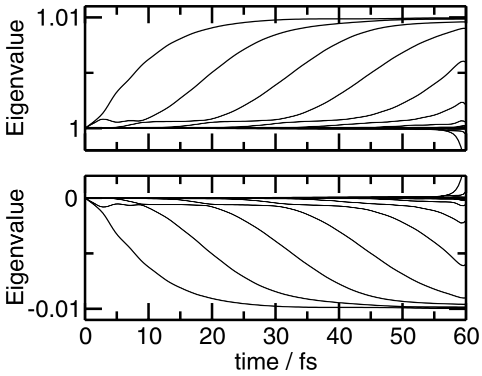

Figure 3. The spectrum of eigenvalues for the single-particle electronic density matrix as a function of time. All the eigenvalues are clumped either about 0 (lower graph) or about 1 (upper graph). A bias of 1 V was used for these plots.

processes are apparent in the quantum kinetic energy (which is consistent with the quantum perturbation treatment [24]). So the present treatment captures the features of both these earlier treatments.

There is, however, a fundamental difference in philosophy between the present treatment and the perturbation treatment. In the perturbation treatment [3, 24] we consider a reference Born–Oppenheimer surface. We then expand the electron–phonon interaction to lowest order in the ionic displacements from equilibrium on that Born–Oppenheimer surface. We treat the unperturbed ionic motion as harmonic, and compute electron–phonon scattering rates to lowest order in the linearized electron–phonon interaction. In the present treatment, no reference Born–Oppenheimer surfaces are invoked, and no assumption about harmonicity is made. The equations of motion are expanded to first order in the ionic fluctuations about the mean trajectory, but the integration of these equations beyond that point is not perturbative.

There is one feature *missing* from the variation of current with time shown in figure 1. In spite of the significant amount of heating, and the consequent broadening of the ionic wavefunctions, there is no obvious reduction in the current which we might expect from increased scattering. We attribute this to the absence of the second, and higher, moments which would introduce the width of the ionic wavefunctions into the equations for the evolution of the electrons. It would also repartition the quantum kinetic energy between quantum kinetic and quantum potential energies. The extension of our correlated electron–ion dynamical equations to second order is the subject of ongoing research.

To achieve the results given above we have made a number of approximations. There is the danger that these approximations may result in the electrons no longer being true fermions. As a check on this possibility, we have evaluated the eigenvalues of the single-particle electronic density matrix during the course of the simulations. If we are treating the electrons as genuine fermions then the eigenvalues must be bounded by 0 and 1. From figure 3 we see that the eigenvalues remain clumped about either 0 or 1. The deviations from these values are very small, so the system of equations does indeed preserve the fermionicity of the electrons.

6. Conclusions

The suppression of ionic heating by an excited electron gas in Ehrenfest dynamics [3] is *not* due solely to the fact that ions are treated classically. Pure classical mechanics, applied to ions *and* electrons, produces the ionic heating that is missing in the Ehrenfest approximation [3] (even though, of course, classical mechanics imposes its own limitations). The key error in

Ehrenfest dynamics is the mean field manner in which the interaction between electrons and ions is treated. In the Ehrenfest approximation, ions interact with the *mean* instantaneous electron density $\rho_{\mathrm{e}}(r, t) = \langle r|\hat{\rho}_{\mathrm{e}}^{(1)}|r\rangle$. The quantity $\rho_{\mathrm{e}}(r, t)$ is an average over the quantum ensemble implicit in the instantaneous electron density matrix. By exposing ions to this ensemble-averaged (though still time-evolving) electron density, Ehrenfest dynamics throws out the microscopic noise in the force exerted by the electrons on the ions, and with it the ionic heating. In that sense, Ehrenfest dynamics effectively replaces the electron gas, as seen by the ions, by a structureless fluid [3]. One way forward might be to seek to introduce correlated force–momentum fluctuations within Ehrenfest dynamics by generating ripples in the fluid. This could be done, for example, by forming electronic wavepackets, or by exposing the electrons to a noisy external field. We have seen in unpublished test calculations that the latter procedure does result in increased ionic heating in current-carrying atomic wires, though not necessarily by the right amount. However, this procedure amounts to an attempt to replace the missing true microscopic electronic noise by macroscopic texture in the quantum probability density that characterizes the electron gas. In other words, it is an attempt to turn the Ehrenfest electron fluid into a gas of quasi-classical lumps, so as to make its dynamical behaviour resemble that of the classical particles. Although this procedure remains a semi-empirical measure, it illustrates a central point: in order to recover electron–ion correlations, one must treat electrons and ions using an internally consistent form of dynamics.

The present paper seeks to establish this internal consistency by retaining the quantum description of electrons while reinstating the quantum nature of ions. This must be done, furthermore, in a way that preserves the electron–ion correlations. Thus, it would not have been sufficient for our purposes to reinstate quantum effects in the ionic motion, while using a mean field description of the electron–ion interaction. Our goal, therefore, has been to introduce tractable dynamical electron–ion correlation functions and corresponding correlation corrections to the Ehrenfest equations of motion.

We note that, while the formalism that we have presented for introducing correlations between dynamical electrons and dynamical ions was originally motivated by the problem of current-induced heating in an atomic wire, for which these correlations had been found previously to be essential [3], it is considerably more general than just this one application. It is founded on a widely applicable assumption, which is that the ionic wavefunctions are narrow. It is this which makes it possible to form an expansion of the combined electron–ion density matrix in terms of powers of fluctuations of the ionic coordinates about a mean trajectory. This expansion significantly simplifies the problem of correlating the electronic and ionic degrees of freedom, but we are still left with a many-body electron problem. To make the problem tractable, we reduce the many-electron problem to a single-electron problem by performing a trace over all the electronic degrees of freedom except one. This introduces both one- and two-electron quantities into the equations of motion. To remove those quantities depending on more than one electron we make a Hartree–Fock-type approximation, and end up with equations that depend solely on single-electron quantities.

Using the first-moment approximation, we performed a number of simulations on a simple system consisting of 701 atoms in a chain of which one was allowed to move. We found that the classical contribution to the kinetic energy exhibits cooling, while the quantum contribution exhibits very much stronger heating. The cooling is independent of the bias, while the heating rate is proportional to the bias. The classical contribution to the kinetic energy behaves very much as it does in the Ehrenfest approximation, while the quantum contribution behaves very much as it does within the quantum perturbation formalism of heating. Thus we find that this approach unifies the two previous approaches. However, it does not introduce increased scattering of electrons as the ions increase their kinetic energy. This effect requires the introduction of at least the second moment so that the electrons can respond to the broadened distribution of the ions.

The similarity between pure classical and pure quantum mechanics in relation to particle correlations, noise and energy dissipation [3] (which is also discernible in other contexts [18]) is an example of corpuscular behaviour in quantum mechanics.

Acknowledgments

CGS and TNT are grateful to EPSRC for support under grant No GR/R36077. DRB acknowledges the Royal Society. Important conversations with, and a critical reading of the manuscript by, Adrian Sutton are gratefully acknowledged.

Appendix

Using a real space representation for the ionic degrees of freedom, equation (3) can be written as

$$\hat{q} = \int \mathrm{d}R\,\mathrm{d}R'\, Q(R, R')\rho_{\mathrm{I}}(R', R)\tilde{\rho}_{\mathrm{e}}(R', R) \tag{A.1}$$

where $\tilde{\rho}_{\mathrm{e}}(R', R) = \hat{\rho}(R', R)/\rho_{\mathrm{I}}(R', R)$, $\hat{\rho}(R', R) = \langle R'|\hat{\rho}|R\rangle$, $\rho_{\mathrm{I}}(R', R) = \mathrm{Tr}_{\mathrm{e}}\{\hat{\rho}(R', R)\}$ and $Q(R', R) = \langle R'|\hat{Q}|R\rangle$. The operator $\tilde{\rho}_{\mathrm{e}}(R', R)$ is an electronic density matrix in the sense that it has the right symmetry properties with respect to interchange of electrons, and satisfies $\mathrm{Tr}_{\mathrm{e}}\{\tilde{\rho}_{\mathrm{e}}(R', R)\} = 1$. If we assume that $\tilde{\rho}_{\mathrm{e}}(R', R)$ varies much more slowly with ionic position than does $\rho_{\mathrm{I}}(R, R')$ (a weak coupling approximation) we can make a Taylor expansion about $\bar{R}$ giving

$$\begin{aligned}
&\hat{q} = \bar{Q}\tilde{\rho}_{\mathrm{e}}(\bar{R}, \bar{R}) + \sum_{\nu}(\overline{Q\Delta R_{\nu}}\tilde{a}_{\mathrm{e},\nu} + \overline{\Delta R_{\nu} Q}\tilde{a}^{\dagger}_{\mathrm{e},\nu}) + \cdots \\
&\overline{Q} = \mathrm{Tr}_{\mathrm{I}}\{\hat{Q}\hat{\rho}_{\mathrm{I}}\} \qquad \tilde{a}_{\mathrm{e},\nu} = \frac{\partial\tilde{\rho}_{\mathrm{e}}(\bar{R}, \bar{R}')}{\partial\bar{R}_{\nu}} \\
&\overline{Q\Delta R_{\nu}} = \mathrm{Tr}_{\mathrm{I}}\{\hat{Q}\Delta\hat{R}_{\nu}\hat{\rho}_{\mathrm{I}}\} \qquad \overline{\Delta R_{\nu} Q} = \mathrm{Tr}_{\mathrm{I}}\{\Delta\hat{R}_{\nu}\hat{Q}\hat{\rho}_{\mathrm{I}}\}.
\end{aligned} \tag{A.2}$$

If we now take traces over electronic degrees of freedom we obtain the following equations:

$$\begin{aligned}
\hat{q}^{(1)} &= \bar{Q}\tilde{\rho}^{(1)}_{\mathrm{e}}(\bar{R}, \bar{R}) + \sum_{\nu}(\overline{Q\Delta R_{\nu}}\tilde{a}^{(1)}_{\mathrm{e},\nu} + \overline{\Delta R_{\nu} Q}\tilde{a}^{(1)\dagger}_{\mathrm{e},\nu}) + \cdots \\
\hat{q}^{(2)} &= \bar{Q}\tilde{\rho}^{(2)}_{\mathrm{e}}(\bar{R}, \bar{R}) + \sum_{\nu}(\overline{Q\Delta R_{\nu}}\tilde{a}^{(2)}_{\mathrm{e},\nu} + \overline{\Delta R_{\nu} Q}\tilde{a}^{(2)\dagger}_{\mathrm{e},\nu}) + \cdots.
\end{aligned} \tag{A.3}$$

We now make the Hartree–Fock approximation for the two-electron density matrix ($\tilde{\rho}^{(2)}_{\mathrm{e}}(12, 1'2') = \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 1')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 2') - \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 2')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 1')$) and obtain

$$\begin{aligned}
\tilde{a}^{(2)}_{\mathrm{e},\nu}(12, 1'2') &= \tilde{a}^{(1)}_{\mathrm{e},\nu}(1, 1')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 2') + \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 1')\tilde{a}^{(1)}_{\mathrm{e},\nu}(2, 2') \\
&\quad - \tilde{a}^{(1)}_{\mathrm{e},\nu}(1, 2')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 1') - \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 2')\tilde{a}^{(1)}_{\mathrm{e},\nu}(2, 1')
\end{aligned} \tag{A.4}$$

and hence

$$\begin{aligned}
\hat{q}^{(2)}(12, 1'2') &= -\bar{Q}(\tilde{\rho}^{(1)}_{\mathrm{e}}(1, 1')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 2') - \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 2')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 1')) \\
&\quad + (q^{(1)}(1, 1')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 2') + \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 1')q^{(1)}(2, 2') \\
&\quad - q^{(1)}(1, 2')\tilde{\rho}^{(1)}_{\mathrm{e}}(2, 1') - \tilde{\rho}^{(1)}_{\mathrm{e}}(1, 2')q^{(1)}(2, 1')) + \cdots.
\end{aligned} \tag{A.5}$$

The final approximation is that two definitions of the density matrix for the electrons are equal, namely

$$\hat{\rho}_{\mathrm{e}} = \mathrm{Tr}_{\mathrm{I}}\{\hat{\rho}\} \approx \tilde{\rho}_{\mathrm{e}}(\bar{R}, \bar{R}) \tag{A.6}$$

which is obtained from equation (A.2) with $\hat{Q} = \hat{1}$.

The Hartree–Fock approximation requires idempotency of the single-particle density matrix, and that its trace be equal to the number of electrons (N). Using equations (A.3) and (16) we get the following idempotency condition:

$$\tilde{a}^{(1)}_{\mathrm{e},\nu} = \tilde{a}^{(1)}_{\mathrm{e},\nu}\hat{\rho}^{(1)}_{\mathrm{e}} + \hat{\rho}^{(1)}_{\mathrm{e}}\tilde{a}^{(1)}_{\mathrm{e},\nu} \tag{A.7}$$

and hence

$$\hat{q}^{(1)} = -\bar{Q}\hat{\rho}^{(1)}_{\mathrm{e}} + \hat{q}^{(1)}\hat{\rho}^{(1)}_{\mathrm{e}} + \hat{\rho}^{(1)}_{\mathrm{e}}\hat{q}^{(1)} + \cdots. \tag{A.8}$$

Now consider the commutator of the first moment $\hat{\mu}^{(2)}_{\nu}$ with the two-particle Hamiltonian

$$\begin{aligned}
\mathrm{Tr}_2\{[\hat{H}^{(2)}_{\mathrm{e}}, \hat{\mu}^{(2)}_{\nu}]\} &= \sum_{1''2''2}\{H^{(2)}_{\mathrm{e}}(12, 1''2'')\mu^{(2)}_{\nu}(1''2'', 1'2) - \mu^{(2)}_{\nu}(12, 1''2'')H^{(2)}_{\mathrm{e}}(1''2'', 1'2)\} \\
&= \sum_{1''2''2}\{H^{(2)}_{\mathrm{e}}(12, 1''2'')(\rho^{(1)}_{\mathrm{e}}(1'', 1')\mu^{(1)}_{\nu}(2'', 2) + \mu^{(1)}_{\nu}(1'', 1')\rho^{(1)}_{\mathrm{e}}(2'', 2) \\
&\quad - \rho^{(1)}_{\mathrm{e}}(1'', 2)\mu^{(1)}_{\nu}(2'', 1') - \mu^{(1)}_{\nu}(1'', 2)\rho^{(1)}_{\mathrm{e}}(2'', 1')) \\
&\quad - (\rho^{(1)}_{\mathrm{e}}(1, 1'')\mu^{(1)}_{\nu}(2, 2'') + \mu^{(1)}_{\nu}(1, 1'')\rho^{(1)}_{\mathrm{e}}(2, 2'') \\
&\quad - \rho^{(1)}_{\mathrm{e}}(1, 2'')\mu^{(1)}_{\nu}(2, 1'') - \mu^{(1)}_{\nu}(1, 2'')\rho^{(1)}_{\mathrm{e}}(2, 1''))H^{(2)}_{\mathrm{e}}(1''2'', 1'2)\}.
\end{aligned} \tag{A.9}$$

If we define the following mean field operators in terms of their matrix elements:

$$\begin{aligned}
H^{(\mathrm{HF})}(1, 1') &= H^{(1)}_{\mathrm{e}}(1, 1') + \sum_{22'}\{H^{(2)}_{\mathrm{e}}(12, 1'2') - H^{(2)}_{\mathrm{e}}(12, 2'1')\}\rho^{(1)}_{\mathrm{e}}(2', 2) \\
I^{(\mathrm{HF})}_{\nu}(1, 1') &= \sum_{22'}\{H^{(2)}_{\mathrm{e}}(12, 1'2') - H^{(2)}_{\mathrm{e}}(12, 2'1')\}\mu^{(1)}_{\nu}(2', 2)
\end{aligned} \tag{A.10}$$

then we obtain

$$[\hat{H}^{(1)}_{\mathrm{e}}, \hat{\mu}^{(1)}_{\nu}] + \mathrm{Tr}_2\{[\hat{H}^{(2)}_{\mathrm{e}}, \hat{\mu}^{(2)}_{\nu}]\} = [\hat{H}^{(\mathrm{HF})}, \hat{\mu}^{(1)}_{\nu}] + [\hat{I}^{(\mathrm{HF})}_{\nu}, \hat{\rho}^{(1)}_{\mathrm{e}}]. \tag{A.11}$$

For $\hat{\lambda}^{(1)}_{\nu}$ we have similarly

$$\begin{aligned}
&[\hat{H}^{(1)}_{\mathrm{e}}, \hat{\lambda}^{(1)}_{\nu}] + \mathrm{Tr}_2\{[\hat{H}^{(2)}_{\mathrm{e}}, \hat{\lambda}^{(2)}_{\nu}]\} = [\hat{H}^{(\mathrm{HF})}, \hat{\lambda}^{(1)}_{\nu}] + [\hat{J}^{(\mathrm{HF})}_{\nu}, \hat{\rho}^{(1)}_{\mathrm{e}}] \\
&J^{(\mathrm{HF})}_{\nu}(1, 1') = \sum_{22'}\{H(12, 1'2') - H(12, 2'1')\}\lambda^{(1)}_{\nu}(2', 2).
\end{aligned} \tag{A.12}$$

The anti-commutator terms in equation (17) involving $\hat{K}^{(0)}_{\nu\nu'}$, $\hat{K}^{(1)}_{\nu\nu'}\hat{\mu}^{(1)}_{\nu}$ and $\hat{\mu}^{(2)}_{\nu}$ combine to give

$$\sum_{\nu'}(-\bar{K}_{\nu\nu'}\hat{\mu}^{(1)}_{\nu'} + \hat{\mu}^{(1)}_{\nu'}\hat{K}^{(1)}_{\nu\nu'}\hat{\rho}^{(1)}_{\mathrm{e}} + \hat{\rho}^{(1)}_{\mathrm{e}}\hat{K}^{(1)}_{\nu\nu'}\hat{\mu}^{(1)}_{\nu'} - \tfrac{1}{2}(\hat{K}^{(1)}_{\nu\nu'}\hat{\mu}^{(1)}_{\nu'} + \hat{\mu}^{(1)}_{\nu'}\hat{K}^{(1)}_{\nu\nu'})) \tag{A.13}$$

where $\bar{K}_{\nu\nu'} = \hat{K}^{(0)}_{\nu\nu'} + \mathrm{Tr}_{\mathrm{e},1}\{\hat{\rho}^{(1)}_{\mathrm{e}}\hat{K}^{(1)}_{\nu\nu'}\}$.

References

[1] Todorov T N 2001 *J. Phys.: Condens. Matter* **13** 10125

[2] Horsfield A P, Bowler D R and Fisher A J 2004 *J. Phys.: Condens. Matter* **16** L65

[3] Horsfield A P, Bowler D R, Fisher A J, Todorov T N and Montgomery M J 2004 *J. Phys.: Condens. Matter* **16** 3609

[4] Montgomery M J, Hoekstra J, Todorov T N and Sutton A P 2003 *J. Phys.: Condens. Matter* **15** 731

[5] Chen Y C, Zwolak M and Di Ventra M 2003 *Nano Lett.* **3** 1691

[6] Brandbyge M, Mozos J L, Ordejon P, Taylor J and Stokbro K 2002 *Phys. Rev.* B **65** 165401

[7] Di Ventra M and Lang N D 2002 *Phys. Rev.* B **65** 45402

[8] Di Ventra M and Pantelides S T 2000 *Phys. Rev.* B **61** 16207

[9] Landauer R 1989 *J. Phys.: Condens. Matter* **1** 8099

[10] Sanvito S, Lambert C J, Jefferson J H and Bratkovsky A M 1999 *Phys. Rev.* B **59** 11936

[11] Taylor J, Guo H and Wang J 2001 *Phys. Rev.* B **63** 245407

[12] Todorov T N 2002 *J. Phys.: Condens. Matter* **14** 3049
[13] Ness H and Fisher A J 1999 *Phys. Rev. Lett.* **83** 452
[14] Ehrenfest P 1927 *Z. Phys.* **45** 455
[15] Messiah A 1961 *Quantum Mechanics* vol 1 (Amsterdam: North-Holland)
[16] Andrews M 1981 *J. Phys. A: Math. Gen.* **14** 1123
[17] Andrews M and Hall M 1985 *J. Phys. A: Math. Gen.* **18** 37
[18] Ballentine L E and McRae S M 1998 *Phys. Rev.* A **58** 1799
[19] Prezhdo O V and Pereverzev Y V 2000 *J. Chem. Phys.* **113** 6557
[20] Brooksby C and Prezhdo O V 2001 *Chem. Phys. Lett.* **356** 463
[21] Prezhdo O V and Pereverzev Y V 2002 *J. Chem. Phys.* **116** 4450
[22] Pahl E and Prezhdo O V 2002 *J. Chem. Phys.* **116** 8704
[23] Parr R G and Yang W 1989 *Density Functional Theory of Atoms and Molecules* (New York: Oxford University Press)
[24] Montgomery M J, Todorov T N and Sutton A P 2002 *J. Phys.: Condens. Matter* **14** 5377
[25] Todorov T N, Hoekstra J and Sutton A P 2001 *Phys. Rev. Lett.* **86** 3606
[26] Tomfor J K and Sankey O F 2001 *Phys. Status Solidi* b **226** 115
[27] Stier W and Prezhdo O V 2002 *J. Phys. Chem.* B **106** 8047