Software for Non-Adiabatic Molecular Dynamics

Daniel Dundas[a*], Daniel Mason[b†], Lorenzo Stella[c‡]
Yu Wang[a], Eunan McEniry[a], Chris Race[b], Rafael Miranda[c],
Andrew Horsfield [b]

[a]Queens University Belfast, [b]Imperial College London, [c]University College London

*d.dundas@qub.ac.uk, †d.mason@imperial.ac.uk, ‡l.stella@ucl.ac.uk

Introduction

A foundational approximation of Molecular Dynamics (MD) is the neglect of non-adiabatic processes. The success of MD in a wide variety of contexts demonstrates just how robust this normally is. However, there are some problems in which the exchange of heat between electrons and nuclei is the whole story [1], and for these we need to modify the formalism of MD to create non-adiabatic MD (NAMD).

The example that caused us and our intrepid colleagues to set off down the rocky road of NAMD is the heating of ions by an electric current in nanowires. If you perform adiabatic MD in the presence of an electric current, then you obviously find no heating of the ions. The question is then: what level of correction is needed? First we investigated the simplest scheme that we were aware of, namely Ehrenfest Dynamics (ED). In ED the electrons evolve according to the time-dependent Schrödinger equation, while the ions evolve classically. But this failed to reproduce the heating of the ions by hot electrons, though it could produce heating of cold electrons by hot ions [2, 3]. This asymmetry exists because each ion is treated explicitly, so their fluctuations are visible to the electrons who can thus identify the ionic temperature. The electrons, on the other hand, are experienced by the ions as a structureless fluid whose temperature cannot be identified through the forces. This is a completely general property of the Ehrenfest approximation, independent of the level of description of the electrons.

At that time there was no non-adiabatic method that both used MD and operated with open boundaries for the electrons, so we set out to devise one. We named the method Correlated Electron-Ion Dynamics, or CEID (pronounced "seed"). To go beyond ED we introduced small *quantum* fluctuations in the ionic trajectories by means of a low order moment expansion [4]. This allows the ions to probe the response of the electrons to small changes in their trajectory from which information about the internal state of the electrons can be determined. The moments correspond to powers of the instantaneous ionic positions and momenta relative to the mean values for the trajectories. The first moment gave us heating, while the second moment was needed to introduce the scattering of electrons by heated ions [5].

Since then we have entered two other fields where non-adiabatic processes are important. The first is radiation damage in metals in which very high energy ions ricochet through crystalline metal, exciting electrons as they go. The Ehrenfest approximation is found to be adequate for this problem because the ions are very energetic and heat the electrons, rather than the other way around. The second field is the response of conjugated polymers to photoexcitation (important in photovoltaics). In order to capture the strong non-adiabatic effects that can take place as the electrons evolve, we had to redesign our formalism, introducing an efficient basis set expansion [6] as the moment expansion could not be extended in a stable manner. We now have a scheme that is very stable and can be extended systematically.

To address the above problems, we have in each case had to develop a substantial new computer code. Below we describe these programs. If you wish to learn more about these programs, or would like to use them as part of a collaboration, you might like to attend a one day meeting to be held at the Institute of Physics on Monday July 13th. Attendance is free, but you need to register so we know how large a lecture theatre we need and how much food to provide. Details of the meeting can be found on the IoP website here. (The URL is given in the acknowledgements at the end.)

spICED

In the limit that spontaneous phonon emission may be neglected, i.e. where the ionic temperature is much greater than the electronic, the Ehrenfest approximation result for the rate of heat transfer between ions and electrons is good [7]. At Imperial College London we have focussed on using the Ehrenfest approximation in a region where it is applicable- to look at high energy ions in metals.

In a radiation damage process, incoming high energy particles collide with the ions of the solid. The primary knock-on atoms (PKAs), hit by the incoming particles, recoil and go on to cause damage themselves. We have had some success assessing the validity of simple empirical models of heat transfer between the hot ions within a displacement cascade and the metallic electrons. An investigation of a single driven oscillating atom within a metal [8] showed that the rate of energy transfer to the electrons is dependent on the electronic temperature, the position of the vibrating atom within the unit cell and even the direction of oscillation. This directly leads to anisotropy in the non-adiabatic forces on ions.

Running Ehrenfest dynamics simulations of the early evolution of low energy displacement cascades has led us to confirm that while a damping force proportional to velocity is sufficient to model the bulk of energy transfer from ions to electrons, a larger rate of energy transfer is seen when the ionic kinetic energy is confined to a focused sequence of collisions [9]. Recently we have also been able to show that electronic excitations generated during a cascade are well described by a Fermi-Dirac distribution at some elevated temperature, even in the absence of the direct electron-electron interactions that would be required in order to thermalize a non-equilibrium distribution [10]. We are now moving on to investigating high energy ion channeling. A high energy ion moving between crystal planes can travel a considerable distance as the principal energy loss mechanism is through electronic stopping; MeV ions beamed at a surface will penetrate to micron depths, allowing subsurface doping. Figure 1 shows snapshots of radiation damage and channeling simulations possible with spICED.

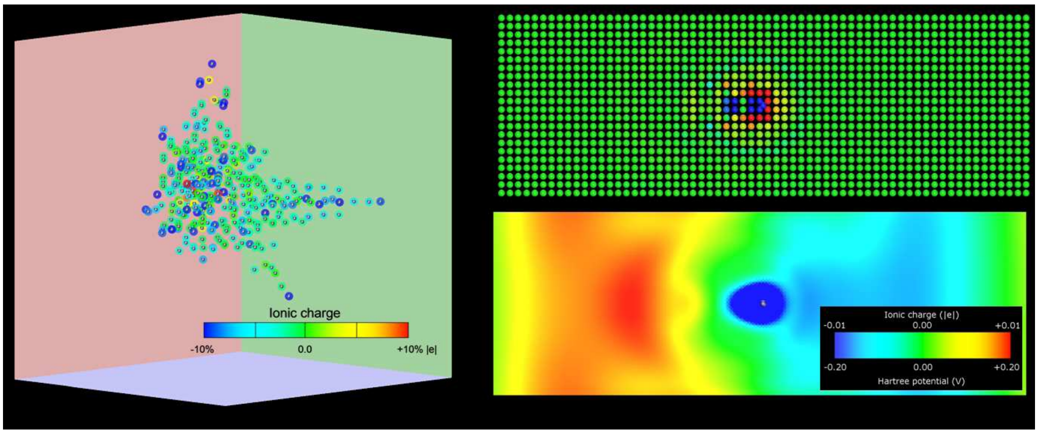

Figure 1: Snapshots from simulations possible with spICED. Left: 100fs into a 1keV cascade in 13440 copper atoms, we see the displaced atoms appear as jets along $\langle 110 \rangle$ directions. This coincides with where the electronic damping is at its greatest. Right: A 1MeV ion moving left-to-right down a $\langle 100 \rangle$ channel in a simulation of 14080 copper atoms is somewhat ahead of the compensating screening charge cloud and leaves a streak of negative charge on the ions it has just passed. The Hartree potential in the plane shows a gradient against the direction of motion, indicating a Coulombic drag on the moving ion.

To generate these results we have developed the spICED (sparse parallel Imperial College Ehrenfest Dynamics) code. This program, primarily designed to run large-scale (tens of thousands of atoms) tight binding dynamical simulations within the Ehrenfest approximation, has been in development for three years and now comprises some eighty thousand lines of code. It has been designed, as far as possible, for flexibility and robustness rather than raw speed. Its modular f95 structure contains many of the elements of expressive programming described here in a previous newsletter [11], with 80 derived types, all with private fields, nested up to 5 layers deep. We have elected to use xml for all input files, linked together with XInclude to generate reusable libraries.

spICED is parallelized with MPI, scaling well to 128 cores on HeCTOR. This scaling performance is acheived by exploiting the predictable sparseness of the Hamiltonian in the atomic basis set. The hopping integral between atoms I and J is zero if the distance between them is greater than some cutoff R_c. Therefore if the atoms are indexed by z-position, and then grouped into slices of thickness greater than R_c then the Hamiltonian becomes block tridiagonal, with block (S, S') linking together atoms in slice S with those in S'. Computing the time derivative of the electronic state with the Quantum Liouville equation requires the commutator of the sparse symmetric Hamiltonian and dense Hermitian density matrix. The commutator for block (S; S′) requires knowledge only of the Hamiltonian and density matrix blocks neighbouring (S; S′). Blocks from the upper triangle of the density matrix are distributed across the processors. An up-to-date halo of neighbouring blocks is then maintained by a local exchange of messages each update step.

Evolving the electrons in a model metal using Ehrenfest dynamics is sufficiently computationally inexpensive that simulations of ten thousand atoms and more are now routine. This opens up the possibility of using simulation cells of a sufficient size to contain the trajectories of high energy atoms; and with this the possibility of exploring radiation damage and other phenomena with proper quantum mechanical electrons. We have been able to study the electronic stopping of ions with a kinetic energy of eV up to MeV, and are now looking at the velocity dependence of the charges of high energy ions in a metal. spICED offers an easy-to-use platform for exploring non-adiabatic processes with tight binding simulations. It could easily be pressed into simulation of semiconductors (by dropping in a new tight binding model); study the response to high electric fields with fifty lines of code, or explore non-adiabatic electronic effects in high energy surface phenomena such as sputtering just by changing an input file. The flexible code structure and good scaling means we have barely scratched the surface of Ehrenfest dynamics simulations.

pDINAMO

The initial motivation for the development of the CEID formalism was the study of electrical conduction in atomic wires. In the last decade, the study of electron transport phenomena in nanoscale devices has undergone spectacular development. Understanding the transport properties of such nanoscale devices is crucial as the size of present day electronic devices approaches the regime where quantum effects dominate their functioning. Experimentally, it has now become possible to make chains of single atoms between two electrodes, pass a current along this chain and study the effects of the current flow on the atoms in the wire [12]. Theoretically, it has become possible to not only calculate how much current flows through an atomic wire, but to make predictions about the local heating of the wire, about forces that the current exerts on individual atoms, and about the critical voltages at which the current blows the wire to pieces [13]. These predictions have been verified experimentally [14]. More recently, a fresh wave of theory has started to focus on the dynamical quantum description, in real time, of current and of the interaction between current-carrying electrons and vibrating ions in nanodevices.

The original code that implemented the CEID equations of motion was called DINAMO (Dynamics In Non-Adiabatic Molecular Orbitals). This serial code was developed in-house at QUB by Dr Cristián Sánchez, now at the University of Córdoba, Argentina. DINAMO solves a tightly coupled set of equations that are currently truncated at second order in electron-ion correlations, as mentioned in the introduction. These equations are propagated in real time for several hundred femtoseconds in order to model the dynamical response of the atoms. It quickly became apparent to us that in order to treat realistic problems, a parallel code was required. To see this, consider first ED. The bottleneck in ED simulations is the quantum evolution of the electronic dynamics, which we handle by solving the quantum Liouville equation. This equation scales as N^2 where N is the number of basis functions used in our description of the electronic subsystem (currently tight binding models are implemented). Compared to this, the algorithmic and memory costs of the second-order CEID equations scale as $(6M + 1)N^2$ where M is the number of dynamic "CEID" ions. Parallelization of DINAMO commenced just over two years ago, resulting in a new code called pDINAMO [15].

The philosophy behind the parallelization of DINAMO is to produce a fully scalable code that runs on a wide range of computer hardware. In light of this the most appropriate parallelization method is a domain decomposition based upon the message passing interface (MPI). DINAMO was originally designed as a layered code whereby an application layer sits on top of a linear algebra layer. pDINAMO extends this design through the addition of a communications layer on which the linear algebra layers sits. Such a design minimizes disruption to the application layer but obviously it is necessary to rewrite the linear algebra layer to make use of parallel methods and algorithms. All linear algebra routines have been hand-coded in pDINAMO to exploit the underlying parallelism except for a number of diagonalization routines (used in preparing an initial state for the simulations) for which we use ScaLAPACK. Two re-engineering phases of pDINAMO have already taken place to improve the performance and scalability of the code (thus increasing the range of problems that can be tackled) and to implement additions to the continuously developing theory (such as open boundary conditions for transport [16]). In order to produce a fully scalable code two levels of parallelization are required: firstly, the distribution of electron-ion correlation matrices (the N^2 scaling); secondly, the distribution of correlation matrices corresponding to different CEID ions (the $6M + 1$ scaling). The code currently implements the first level of parallelization. This places a limit on the number of CEID ions we can treat. For instance, when $N = 3000$ we have $M \leq 12$ whereas when $N = 10000$ we have $M \leq 3$. Implementation of the second level of parallelization is currently underway and will allow us to treat a larger number of moving CEID ions for a given N. Currently, pDINAMO runs on a wide range of hardware ranging from desktop computers to the HPCx and HECToR national services.

CEID, as implemented in pDINAMO, has been applied to a number of problems in transport. In addition it has been compared with other established methods such as the Self-Consistent Born Approximation [18]. As well as implementing the CEID equations of motion at the second moment level, pDINAMO also implements ED as a zeroth-moment approximation. We have recently used pDINAMO at the Ehrenfest level to study the effect of current-induced forces on electron transport. After showing mathematically that current-induced forces are not conservative we demonstrated, through dynamical simulation, that these forces provide a new mechanism for energy transfer from electrons to ions. This mechanism, which differs fundamentally from Joule heating, can be gauged to do useful work on atoms. It thus provides the basis for the ultimate atomic-scale motor, in which current flow drives and accelerates a single atom in a circular orbit, creating an elemental waterwheel [17]. In these simulations we considered a bent atomic chain with the corner atom allowed to move. The dynamical response of this atom was then investigated using a nearest-neighbour single-orbital

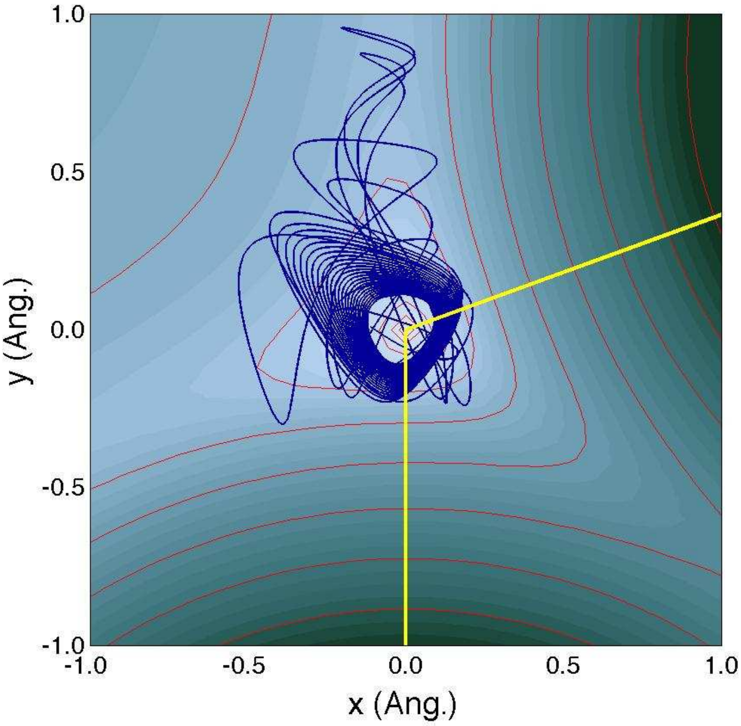

Figure 2: Current-induced response of the corner atom in our bent atomic wire. A 601-atom chain (yellow), initially aligned along the vertical (y) axis is considered. Those atoms aligned along the positive y-axis are then rotated by an angle of 70^o as shown. An electro-chemical potential difference of magnitude 1V is applied across the chain using our open boundary method and the response of the corner atom is studied over a timeframe of 5 picoseconds (ps). The trajectory traced by the moving atom (blue) is shown together with a plot of the ground-state potential energy surface on which the corner atom moves. The red lines denote equipotential surfaces. For clarity the trajectory is traced over the simulation time 2.0–2.7ps. Further simulation details can be found in Ref. [17]

orthogonal tight binding model (simulation details can be found in Ref. [17]). While the waterwheel effect was uncovered in the simulations, this required specially tuned conditions even for one moving atom. Two factors caused this sensitivity. First, in general the two independent Einstein frequencies of the corner atom in the plane of the bent chain are unequal which means that the ground-state potential-energy surface (PES) has an easy and a hard axis. This leads to self-crossing trajectories in which the non-conservative force does little or no net work. The second factor is the displacement of the atom from the harmonic minimum, due to the current-induced force, which additionally complicates the motion. After many parameter searches we were able to locate both a bend angle for the chain and specific onsite energies for the moving atom and its neighbours that minimized these two effects: with these adjustments the new ground-state PES had approximately equal frequencies and the displacement of the atom by the current was still within the harmonic part of the PES. Figure 2 shows the ground-state PES obtained for a 601-atom chain together with the trajectory traced out by the corner atom when an electro-chemical potential difference of magnitude 1V is applied across the chain. The nanowheel undergoes a series of cycles, in which the kinetic energy rises and falls. As the orbit grows, the atom eventually leaves the harmonic part of the well. The motion becomes erratic, the electronic friction in ED (together with the non-conservative force which can now act as a brake) brings the kinetic energy down, and the cycle starts again.

PolyCEID

PolyCEID is a computer code written in C to test a new version of CEID appropriate for molecules. Indeed, in small systems one can expect quantum coherence between electrons and ions to play a particularly relevant role. In principle, in order to deal with subtle coherence effects, one has to resort to a higher truncation order of the original CEID hierarchy. This was not possible within the original version of CEID, which employs a truncation scheme based on density matrix moments [5]. Therefore a new approach based on a direct expansion of the complete density matrix (electrons and ions) has been devised, tested, and finally implemented in a computer code — PolyCEID — to solve this issue.

The main idea behind this new version of CEID is to expand the quantum fluctuations of ions about their mean-field (or Ehrenfest) trajectories [6]. Since ionic wavefunctions are usually well localised — with the possible relevant exception of protons — about their trajectories, one expects the approximation made by truncating small wavelength fluctuations to be appropriate. Indeed, the lowest order truncation of the CEID hierarchy is equivalent to Ehrenfest dynamics, which is known to produce reliable results in many, yet not all, cases (see above). Therefore, by increasing the order of the truncation in a systematic way, one expects to find better and better agreement with the exact evolution given by the solution of the time-dependent Schödinder equation.

In order to test the convergence of the new CEID approach we originally considered simple two-level systems (2LS) depending on a single ionic coordinate. Although extremely simplified, this model allows one to study dynamical effects beyond the mean-field approach, i.e., Ehrenfest Dynamics. A quick comparison between the electronic level populations in the upper and lower left panels of Fig. 3 shows that a CEID order 5 simulation (panel (b)) is already converged with respect to both the exact solution (panel (a)) and higher CEID order simulations (a 10th order one is reported in panel (a)). Surprisingly, a CEID order 0 simulation completely fails to reproduce the oscillating behaviour of the electronic level populations. We can say, in analogy with quantum electrodynamics, that the spontaneous emission of *phonons* is completely missed by Ehrenfest dynamics since in that framework atoms are completely classical. As a consequence, an excited electron misses a possible decay channel which turns out

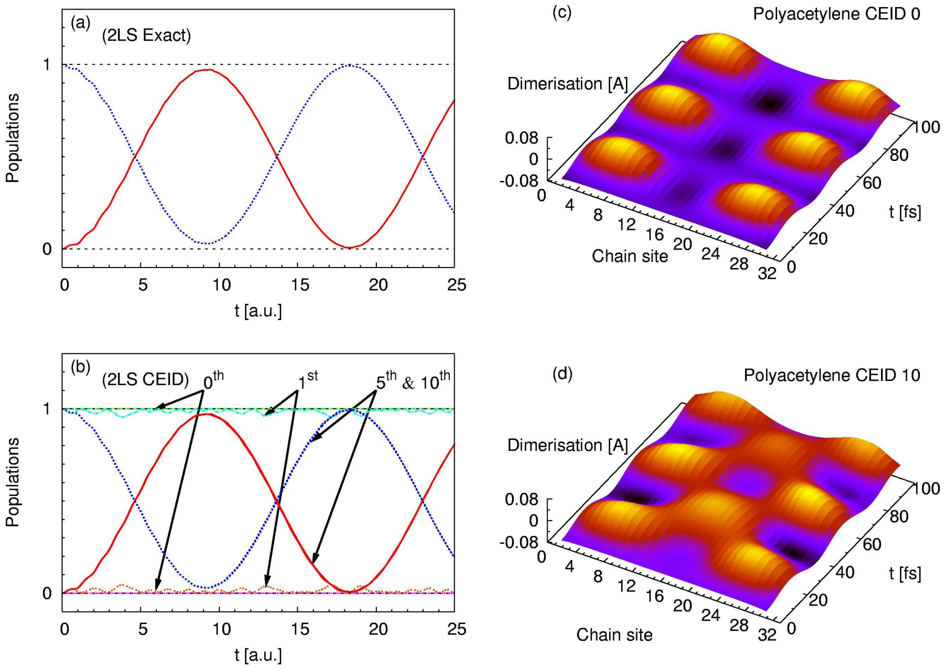

Figure 3: PolyCEID findings: Left panels, results for a resonant two-level system displaying a Landau-Zener transition. Panel (a) shows the evolution of the electronic populations acoording to the exact solution of the time-dependent Schrödinger equation. The 2LS is initially prepared in its excited state. In panel (b) population dynamics from CEID simulations of order 0, 1, 5, and 10 are reported. Right panels, dimerization dynamics for a tight binding model of the finite Polyacetylene chain $CH_2[C_2H_2]_{16}CH_2$. Panel (c) shows the evolution predicted by a CEID order 0 simulation (equivalent to Ehrenfest dynamics). In panel (d) are reported results given by a CEID order 10 simulation.

to be the crucial one in the simple 2LS under inspection.

Of course, quantum coherence between electrons and ions can play an important role also in more realistic molecular models. On the other hand, since one expects decoherence time to be shorter for systems containing many atoms, one can confine his investigation to very short time scales, of the order of few hundreds of femtoseconds, corresponding to very few molecular oscillations. To test the new CEID approach in this range of scales, we studied a tight binding model parametrized to reproduce the dynamics of excited polyacetylene chains. In this case, despite the absence of an explicit electron-electron interaction term in our quadratic Hamiltonian, we made use of a truncated CI expansion to properly describe the electronic degrees of freedom of the system. Indeed, although the ground-state is well described by a single Slater determinant, a longer many-body expansion is needed in order to reproduce the non-adiabatic evolution of an excited state. The truncation of the CI expansion is chosen by taking into account the energy of the excitations (by introducing a cutoff) and the relative contribution of the single molecular orbitals (by using a limited active space).

Once again, we found that by including some amount of quantum fluctuations of ions, i.e., by setting a non-zero CEID order in our simulations, the predicted behaviour of the chain dynamics dramatically changes [19]. In the right panels of Fig. 3 the plot of the dimerization parameter $D_i = (-)^i(R_{i+1} - 2R_i + R_{i-1})/4$ where R_i is the (averaged) position of the i-th atom of the chain, is reported for the first 100 fs. The dimerization parameter is the order parameter for this kind of one-dimensional systems and in some extent it measures the local distortion of a (dimerized) chain. A larger distortion is the fingerprint of localised excitations like excitons and polarons. One can easily see from a comparison between panel (c) (CEID order 0) and panel (d) (CEID order 10) of Fig. 3 the dramatic effect of the electron-ion correlations on the chain dynamics. The two well separated "pockets" in the dimerization plot can merge in a single "pocket" during a high order, converged CEID simulation (lower right panel) at variance with the relatively trivial results of an Ehrenfest like (i.e., CEID 0) simulation (upper right panel). This is another manifestation of a new decay channel opening due to the excitability of ionic quantum degrees of freedom (i.e., spontaneous emission of phonons), in agreement with what we found for a simple 2LS. We are currently investigating the role of these electron-ion correlation effects in the production rate of photo-carriers in conjugated polymers, which is a sensitive parameter in designing better performing organic solar cells.

In summary, the new CEID approach developed at UCL has been proved to be appropriate for describing coherent electron-ion effects, especially electronic decay triggered by spontaneous emission of phonons. We focused so far only on model systems in order to test this new approach, but we are now moving to a better treatment of the Coulomb interaction, possibly by post-Hartree-Fock methods. The final goal of our effort is to provide a tool to study the effects of the electron-electron and electron-phonon interactions at the same time in order to improve the description of non-adiabatic processes in realistic molecular systems.

Acknowledgements

This work was carried out in collaboration with Tchavdar Todorov, Cristián Sánchez, David Bowler, Andrew Fisher, Marshall Stoneham, Adrian Sutton, Jonathan le Page, Matthew Foulkes, and Mike Finnis.

The meeting web page URL is:
`http://www.iop.org/Conferences/Forthcoming_Institute_Conferences/Correlated%20Electron-Ion%20Dynamics_Debutante/page_32107.html`

References

[1] A. P. Horsfield, D. R. Bowler, H. Ness, C. G. Sànchez, T. N. Todorov, and A. J. Fisher. The transfer of energy between electrons and ions in solids. *Rep. Prog. Phys.*, 69:1195–1234, 2006.

[2] A. P. Horsfield, D. R. Bowler, and A. J. Fisher. Open-boundary Ehrenfest molecular dynamics: towards a model of current induced heating in nanowires. *J. Phys.: Condens. Matter*, 16:L65, 2004.

[3] A. P. Horsfield, D. R. Bowler, A. J. Fisher, T. N. Todorov, and M. J. Montgomery. Power dissipation in nanoscale conductors: classical, semi-classical and quantum dynamics. *J. Phys.: Condens. Matter*, 16(21):3609–3622, 2004.

[4] A. P. Horsfield, D. R. Bowler, A. J. Fisher, T. N. Todorov, and C. Sànchez. Beyond Ehrenfest: correlated non-adiabatic molecular dynamics. *J. Phys.: Condens. Matter*, 16(46):8251–8266, 2004.

[5] A. P. Horsfield, D. R. Bowler, A. J. Fisher, T. N. Todorov, and C. G. Sànchez. Correlated electron-ion dynamics: the excitation of atomic motion by energetic electrons. *J. Phys.: Condens. Matter*, 17:4793–4812, 2005.

[6] L. Stella, M. Meister, A. J. Fisher, and A. P. Horsfield. Robust non-adiabatic molecular dynamics for metals and insulator. *J. Chem. Phys.*, 127:214104, 2007.

[7] J. le Page, D. R. Mason, and W. M. C. Foulkes. The Ehrenfest approximation for electrons coupled to a phonon system. *J. Phys.: Condens. Matter*, 20:125212, 2008.

[8] D. R. Mason, J. le Page, C. P. Race, W. M. C. Foulkes, M. W. Finnis, and A. P. Sutton. Electronic damping of atomic dynamics in irradiation damage of metals. *J. Phys.: Condens. Matter*, 19:436209, 2007.

[9] J. le Page, D. R. Mason, C. P. Race, and W. M. C. Foulkes. How good is damped molecular dynamics as a method to simulate radiation damage in metals? *New J. Phys.*, 11:013004, 2009.

[10] C. P. Race, D. R. Mason, and A. P. Sutton. Electronic excitations and their effect on the inter-ionic forces in simulations of radiation damage in metals. *J. Phys.: Condens. Matter*, 21:115702, 2009.

[11] G. Csányi et al. Expressive programming for computational physics in Fortran 95+. *IOP Comp. Phys. Group Newsletter*, Spring, 2007.

[12] A. I. Yanson, G. Rubio Bollinger, H. E. van den Brom, N. Agraït, and J. M. van Ruitenbeek. Formation and manipulation of a metallic wire of single gold atoms. *Nature*, 395:783–785, 1998.

[13] T. N. Todorov, J. Hoekstra, and A. P. Sutton. Current-induced embrittlement of atomic wires. *Phys. Rev. Lett.*, 86:3606–3609, 2001.

[14] M. Tsutsui, S. Kurokawa, and A. Sakai. Bias-induced local heating in au atom-sized contacts. *Nanotechnology*, 17:5334–5338, 2006.

[15] D. Dundas, E. J. McEniry, D. Mason, and L. Stella. Modelling non-adiabatic processes in materials with correlated electron-ion dynamics. *Capability Computing*, 10:12–14, 2008.

[16] E. J. McEniry, D. R. Bowler, D. Dundas, A. P. Horsfield, C. G. Sánchez, and T. N. Todorov. Dynamical simulation of inelastic quantum transport. *J. Phys.: Condens. Matter*, 19:196201, 2007.

[17] D. Dundas, E. J. McEniry, and T. N. Todorov. Current-driven atomic waterwheels. *Nature Nanotechnology*, 4:99–102, 2009.

[18] E. J. McEniry, T. Frederiksen, T. N. Todorov, D. Dundas, and A. P. Horsfield. Inelastic quantum transport in nanostructures: The self-consistent Born approximation and correlated electron-ion dynamics. *Phys. Rev. B*, 78:035446, 2008.

[19] L. Stella. To be published. 2009.

Dr Andrew Horsfield is working at the Imperial College London and can be contacted at A.Horsfield@imperial.ac.uk