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Non-adiabatic dynamics of electrons and atoms under non-equilibrium conditions

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Abstract

An approach to non-adiabatic dynamics of atoms in molecular and condensed matter systems under general non-equilibrium conditions is proposed. In this method interaction between nuclei and electrons is considered explicitly up to the second order in atomic displacements defined with respect to the mean atomic trajectory, enabling one to consider movement of atoms beyond their simple vibrations. Both electrons and nuclei are treated fully quantum-mechanically using a combination of path integrals applied to nuclei and non-equilibrium Green's functions (NEGF) to elections. Our method is partition-less: initially, the entire system is coupled and assumed to be at thermal equilibrium. Then, the exact application of the Hubbard-Stratonovich transformation in mixed real and imaginary times enables us to obtain, without doing any additional approximations, an exact expression for the reduced density matrix for nuclei and hence an effective quantum Liouville equation for them, both containing Gaussian noises. It is shown that the time evolution of the expectation values for atomic positions is described by an infinite hierarchy of stochastic differential equations for atomic positions and momenta and their various fluctuations. The actual dynamics is obtained by sampling all stochastic trajectories. It is expected that applications of the method may include photo-induced chemical reactions (e.g. dissociation), electromigration, atomic manipulation in scanning tunneling microscopy, to name just a few.

1 Introduction

There are a very large number of phenomena in physics, chemistry and biology in which it is necessary to consider non-adiabatic dynamics of system atoms. Prominent examples include, e.g. in biology and chemistry: photosynthesis [1, 2], vision [3, 4], photoisomerization of rhodopsin and isorhodopsin [5], molecular photochemistry of biomolecules [6], proton [7, 8, 9] and electron transfer [10, 11, 12, 13] reactions, also between distant redox centres [14]. Non-adiabatic dynamics is often essential in energy production (photovoltaics) [15, 16], in photo-induced dissociation [17, 18] and isomerisation [19] dynamics, in femtosecond chemistry [20, 21], oxygen production in comets [22], acceleration of urethane and polyurethane formation due to vibrational excitation [23], etc. In physics non-adiabatic effects are also widespread and may be highly important, e.g., in vibrationally promoted electron emission from a metal surface [24], dynamics of nanoparticles under strong laser pulses [25], coupling of plasmons and vibrations in nanoparticles [26], electromigration [27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38] that can adversely affect the nanodevices due to atomic rearrangement leading to their subsequent degradation [39, 40], local heating in a conductor (e.g., in atomic wires) [41, 42, 43, 44, 45, 46], photoelectron spectroscopy [47], radiation damage [48], and atomic manipulation is scanning tunneling microscopy [49, 50, 51, 52], to name just a few.

A considerable number of theoretical tools have been developed over the years to tackle this kind of problems where dynamics of both electrons and nuclei is considered simultaneously. These methods can be crudely divided into two big classes: (i) wave-functions based methods applicable at zero temperatures, and (ii) density matrix based methods which can be applied at any temperature.

In the simplest mixed quantum-classical Ehrenfest approach, within the first class of methods, the nuclei are treated classically (they satisfy classical equations of motion) while electronic wavefunction is evolved in time via the time-dependent Schödinger equation [53]. If transitions between different potential energy surfaces (PES), e.g. due to an optical excitation (and after it upon relaxation), are required to consider, the simplest strategy is offered by the fewest switches surface hopping method [54, 55], in which regions near conical intersections of the PESs along the adiabatic trajectory are branched in a certain way. The advantages and (many) disadvantages of this approximate method are critically discussed in the reviews [56, 57].

We note that there is also a method in which the evolution of the electronic subsystem is replaced by the dynamics of a system of fictitious harmonic oscillators; this enables one to run molecular dynamics simulations of non-adiabatic processes entirely classically. A "quantization" of the electronic states is added approximately. Some successes of this method are reviewed in [58].

An expression for the atomic forces *due to electrons* is required to couple classical equations of motion for atoms and time evolution of the electronic wavefunction. Usually, the force on the classical atomic degree of freedom A in the quantum-classical approaches is calculated via an expression $F_A^e = -\langle \psi_t | \partial_{x_A} H_e | \psi_t \rangle$ with H_e being the electronic Hamiltonian (that includes interaction with nuclei) and ψ_t the corresponding many-electron wavefunction [59, 60, 31, 61, 62, 56, 57] (or the density matrix for the electrons [63]). Since only the potential energy of interaction between nuclei and electrons, V_{ne}, in H_e actually depends on the atomic positions x_A, one gets $\partial_{x_A} H_e \equiv \partial_{x_A} V_{ne}$, and so the above expression for the force then formally coincides [64] with the Hellman-Feynman force normally used in density functional calculations [65, 66]. Note that a proper definition of this force is essential, especially under non-equilibrium conditions, and not in all cases it can be assigned simply to the gradient of the potential energy. Indeed, for instance, at the current flow conditions (e.g., in molecular junctions and nanodevices), when open boundary conditions are used, the number of electrons is not well defined, and hence the potential energy. This problem is formally solved by appealing to the original (and formally exact) Ehrenfest equations [67, 65, 68], which, if written for zero temperature, are:

$$m_A \partial_t \langle x_A \rangle_t = \langle p_A \rangle_t \ , \quad \partial_t \langle p_A \rangle_t = F_A^e + F_A^i = -\langle \partial_{x_A} V_{ne} \rangle_t + F_A^i$$

where F_A^i is the contribution to the total force due to direct interaction between atoms. In these equations the averages $\langle \ldots \rangle_t = \langle \Psi_t | \ldots | \Psi_t \rangle$ are assumed with the wavefunction Ψ_t for the combined electron-nuclear system, so replacing in the expression of the force Ψ_t with ψ_t may seem, although intuitively appealing, still an approximation. In fact, it can easily be shown that this result is exact if it is assumed, within the model of classical nuclei, that the electron-nuclear interaction is described by the integral $\int n_e(\mathbf{r}) \widehat{v}_{ne}(\mathbf{r}) d\mathbf{r}$, where $n_e(\mathbf{r})$ is the electron density and $\widehat{v}_{ne}(\mathbf{r})$ the one-electron potential provided by the nuclei [68]. Indeed, in this case this term contributes, in the Lagrangian equations of motion (with atoms treated classically), a contribution

$$\int n_e(\mathbf{r}) \left(-\partial_{x_A} \widehat{v}_{ne}(\mathbf{r}) \right) d\mathbf{r} \equiv -\langle \psi_t | \partial_{x_A} V_{ne} | \psi_t \rangle$$

which is exactly the contribution employed in quantum-classical approaches. Note that the atomic force thus defined has non-zero curl and hence is not conservative, as may be anticipated [31, 60].

The next, more sophisticated class of methods, still based on the wavefunction treatment of the electronic subsystem, uses Gaussian wave packets (GWP) to represent the nuclei wavefunction [69, 70]. The PESs in these methods are calculated "on the fly" which is efficient. There are several variants of this method: trajectory surface hopping (TSH) [54, 55, 71], coupled coherent states (CCS) [72], *ab initio* multiple spawning (AIMS) [73], multi-configurational Ehrenfest (MCE) [53], *ab initio* multiple cloning [74], and variational multiconfigurational Gaussian wavepacket (vMCG) [75, 76], the latter being more flexible than the others (the parameters of the wavepackets are determined "on the fly" as well), can describe tunneling, but it is also more expensive and numerically more difficult to handle [70]. The multi-configuration time-dependent Hartree (MCTDH) [77, 78, 79] method can be considered as a generalization of the previously mentioned methods that use Gaussian basis, as in MCTDH the nuclear basis is more general. Although these methods, especially their generalised variants vMCG and MCTDH, may provide (in the limit of the complete basis set) an exact solution of the electron-nuclear time-dependent Schödinger equation, the methods are quite expensive computationally and can only be applied to small systems (a small number of nuclear degrees of freedom).

E. K. U. Gross *et al.* have developed a reformulation of the exact time-dependent Schödinger equation in which the wavefunction of the combined system is factorised in the Born-Oppenheimer (BO) form as a product of two variational functions: one for electrons, which depends on the nuclear positions, and one for nuclei [80, 81, 82]. The two equations for each of the wavefunctions are coupled by a scalar and vector potentials that are subject to some gauge conditions. The two equations are strictly equivalent to the original Schödinger equation, and hence are not easier to solve. One advantage of this method is based on the fact that the wavefunction is not expanded into BO electronic wavefunctions for each electronic state, and hence PES for each such a state does not appear. Instead, an effective PES is introduced (the mentioned scalar potential), which corresponds to an *effective propagation* of the system in time. This proved to be useful in analyzing results of the dynamics simulations. The other advantage of this method is that it allows introducing approximations in a more controlled way. Various approximate incarnations of this method have been applied to a number of applications (see, e.g., [83, 84]), demonstrating that the method is very promising.

Concerning density matrix based methods, a number of approaches exist varying in underlying approximations and the cost of the calculations. In quantum-classical Liouville equation (QCLE) method [85, 86, 87, 88] the most important degrees of freedom are treated quantum mechanically (called "the open system"), while the rest of the variables ("the bath") are treated approximately as semi-classical. The latter is done by, first, transforming the Liouville equation using the Wigner transform with respect to the bath variables and then making an expansion in the power series with respect to $\hbar$. In the first order an intuitively expected result is obtained for the transformed Liouville operator that becomes a simple sum of (symmetrised) classical and quantum Poisson brackets [89, 90, 91, 92, 93, 94]. This approach enables one to obtain an approximate equation of motion for the reduced (with respect to the bath degrees of freedom) open system density matrix; the classical variables are evolved in time classically. In the generalized quantum master equation (GQME) method [86] the classical bath degrees of freedom are projected out from the Liouville equation using Nakajima-Zwanzig projection operators, and then the partitioned approach is applied to obtain a self-contained equation for the reduced density matrix of the system. This equation has the form of the first order differential equation with an integral memory term. Then approximations are applied to the calculation of the kernel in the memory term. The partitioned approach assumes the density matrix at the initial time is factorised into a direct product of independent density matrices of the system and bath, i.e. the whole system is initially decoupled. Moreover, the bath is assumed to be at thermal equilibrium. A more general approach that can treat the initial system-bath coupling was developed in [95]. It is argued in [86, 96] that if in QCLE only short time evolutions are accessible, the main advantage of the GQME approach is that one can access relatively longer time scales in the dynamics.

Another way to consider both nuclei and electrons quantum-mechanically is based on path integrals. The most popular are two approaches, the ring-polymer molecular dynamics (RPMD) [97, 98] and centroid molecular dynamics (CMD) [99, 100]. In both methods the starting point is the imaginary time path integral representation of the partition function for the nuclear system associated, initially, with the (single) ground state PES that could be calculated, for instance, with advanced *ab initio* electronic structure methods like density functional theory (DFT). Then the mapping between the Hamiltonian in the Euclidean action of the path integral and that of a ring polymer is exploited that enables one to run "classical" molecular dynamics simulations in extended phase space. The method is very efficient and can be applied to systems containing hundreds of atoms. If initially these methods were only applied to an adiabatic dynamics on a single PES, its extensions to non-adiabatic dynamics have also been proposed, both for RPMD [101, 102, 103, 104, 105] and CMD [106, 107] incarnations. The main limitation of the above methods is that they are designed only for equilibrium; one cannot use these methods for investigating time-dependent and non-equilibrium phenomena, although non-equilibrium situations have also started to be addressed [108].

The methods reviewed so far were derived at different levels of theory and using various approximations. Amongst the wavefunction based methods, approaches based on GWPs are still computationally expensive and can only be applied to relatively small systems. The computationally cheap Ehrenfest based methods with hoppings have a number of shortcomings which cannot be controlled. The method developed in the Gross' group, although theoretically elegant, if applied directly without any approximation, is computationally expensive; only its approximate variants can be used to study realistic systems. A definite advantage of this method is that it is not based on the adiabatic PES. Non-zero temperature methods based on solving the Liouville equation are all approximate, treating nuclei semi-classically. Finally, the path integral based approaches cannot be directly applied to non-equilibrium phenomena. Neither of the previously considered techniques is universal; for instance, it is not obvious how they can be used for problems that require open boundary conditions (e.g. to study current carrying molecular junctions).

A systematic approach that can be applied to a wide class of problems, including the ones with open boundary conditions, has also been developed called the correlated electron-ion dynamics (CEID) [109]. In the initial formulation of the method [110, 111] the Hamiltonian is expanded in a Taylor series with respect to the atomic displacements $u_A = x_A - \langle x_A \rangle_t$ from the mean atomic trajectories $\langle x_A \rangle_t = \text{Tr} \left(\hat{\rho}(t) x_A \right)$ (where $\hat{\rho}(t)$ is the density matrix of the entire system at time t), then various correlation functions appear corresponding to fluctuations of positions, u_A, and momenta $\Delta p_A = p_A - \langle p_A \rangle_t$, for which equations of motion are derived as well. This procedure leads to an infinite hierarchy of first order differential equations which is terminated at a certain order. In [112, 113] an entirely new formulation of the method has been developed based on Wigner transform, which enables one to derive the CEID equations up to an arbitrary order in a systematic way. The main difficulty of the CEID methods, in our view, is related to the fact that it deals directly with the electronic density matrix. As a result, certain approximations (e.g. Hartree-Fock) for it are inevitable to facilitate the solution of the CEID equations.

In principle, this difficulty is circumvented in field-theoretical methods in which electrons are treated via many-body Green's functions (see, e.g., [114]); the Green's functions represent a more convenient tool than the electronic (reduced) density matrix itself involved directly in CEID. The Green's functions based techniques have been for a

long time applied to treating interacting electron-nuclear (in fact, electron-phonon) systems at equilibrium [65, 115, 116, 117]. To study non-equilibrium phenomena, such as, e.g., the effect of phonons on quantum transport through a molecular junction [65, 118] or carrier dynamics in semiconductors [119], one has to consider non-equilibrium techniques based on non-equilibrium Green's functions (NEGF) [120, 121, 122]. These methods are very useful and powerful in calculating, e.g., electronic densities (occupations), currents and phonon spectra at general non-equilibrium conditions and for a wide class of systems with either open or periodic boundary conditions. Their main limitation, however, as far as our main goal here is concerned, is that they can only be used in calculating observables which are expressed via an even number of field (or creation and annihilation) operators, such as, e.g., the electronic density and current. However, they are not suitable for calculating atomic trajectories as atomic positions are linear in field operators; hence, atoms are simply assumed to oscillate around their equilibrium positions in these methods.

In this paper we propose a general non-zero temperature method which enables one to establish quantum "equations of motion" for the expectation values of atomic positions, $\langle x_A \rangle_t$, i.e. their mean trajectory, for arbitrary electron-nuclear system with either periodic or open boundary conditions. The notion of the PES is not invoked here, which we consider an advantage. In this method, at variance with the CEID, electronic NEGF is employed instead of the electronic reduced density matrix, which enables one to apply this method at well known levels of approximation [122] to a wide class of non-equilibrium phenomena and virtually any system, ranging from molecules to condensed phases and molecular junctions. The obtained equations of motion have a stochastic form, i.e. they contain three types of Gaussian noises which are correlated with each other in a certain way via the electronic NEGF. Our method originates from a few powerful ideas that were put forward a long time ago by Hedegård [123] and then recently extended to current carrying molecular junctions in [45], that allowed to express the reduced density matrix of nuclei in the coordinate representation via a partial path integral taken with respect to the nuclear subsystem, while the electronic subsystem is presented via an influence functional with the electronic NEGF (defined in a slightly more general way than usual). In these papers the *partitioned approach* for the initial density matrix (at time t_0) of the combined system was assumed ($\widehat{\rho}(t_0)$ is a direct product of the density matrices of electrons and nuclei) corresponding physically to the two subsystems being completely decoupled initially. Also, the method used in [45] to obtain equations of motion for atoms from the path-integral representation of the nuclei reduced density matrix was largely intuitive. The approach we propose here is a significant generalization and extension of this method. In detail, several important advances have been made: (i) we do not assume that initially the electronic and nuclei subsystems were decoupled; instead, we assume that the whole combined system was at thermal equilibrium, so that time-dependent phenomena can in principle be considered including the transient effects (e.g. switch on of the bias [124]); (ii) the path integral method employed here is also considered as an intermediate tool; however, the passage from the path integrals to the equations of motion for the mean atomic positions is done rigorously, leading to an infinite hierarchy of stochastic differential equations for atomic positions and momenta and their various fluctuations, similarly in spirit to the CEID equations; (iii) by employing an expansion of the electron-nuclear interaction term around the mean atomic trajectory, similarly in spirit to CEID and Ref. [125], which was done up to the second order, we are able to consider a general non-equilibrium situation, whereby atoms do not merely oscillate around their equilibrium positions, but may move along more general trajectories (e.g. as in photo-induced dissociation reactions or during STM manipulation).

In the coming sections we shall present the complete formulation of the main equations of the method and the necessary detailed derivations. No implementation and calculations with this method are yet available and hence will not be presented here; this is left for future work.

2 Theory

2.1 Hamiltonian

At initial time t_0 the entire system (electrons and nuclei) is assumed to be at thermal equilibrium with temperature T, and described by the initial Hamiltonian

$$\mathcal{H}^0 = \mathcal{H}_1^0(x,p) + \mathcal{H}_2^0 + \mathcal{H}_{12}^0(x) \tag{1}$$

where $\mathcal{H}_1^0$ describes the nuclear subsystem to be considered explicitly with coordinates and momenta $x = \{x_A\}$ and $p = \{p_A\}$ (with A designating an nuclear degree of freedom), $\mathcal{H}_2^0$ is the Hamiltonian of the electrons in the whole system, and $\mathcal{H}_{12}^0$ describes the electron-nuclear interaction. We only show explicitly the dependence of the Hamiltonian on the nuclear coordinates and momenta. Note that although interaction of all nuclei with electrons is taken into account, not all nuclei may be allowed to displace from their equilibrium positions; only those allowed to move are explicitly included in the subsystem (or region) 1 and hence presented in the part $\mathcal{H}_1^0(x,p) + \mathcal{H}_{12}^0(x)$ of

the Hamiltonian and therefore included in x. For instance, in the case of a molecule interacting with an external field we may consider all its atoms to be allowed to displace, and in this case their displacements will be considered explicitly. In the case of a molecular junction only atoms in the central region may be considered explicitly; all other atoms belonging to the leads will be frozen and not included in x. The sum of the last two operators, $H_2^0 = \mathcal{H}_2^0 + \mathcal{H}_{12}^0(x)$, constitutes the electrons-only Hamiltonian (for which we shall adopt the second quantization later on). No assumptions are made concerning the form of the nuclear-only, $\mathcal{H}_1^0$, and electron-only, $\mathcal{H}_2^0$, Hamiltonians at this stage, they could be as complex as required.

The Hamiltonian of the whole system at later times $t > t_0$ can be split in a similar way,

$$\mathcal{H} = \mathcal{H}_1(x,p) + \mathcal{H}_2 + \mathcal{H}_{12}(x) \tag{2}$$

and it does not need to coincide with $\mathcal{H}^0$, as it may depend explicitly on time, e.g. due to an external field contained in $\mathcal{H}_1 + \mathcal{H}_2$.

The interaction between electrons and nuclei that are free to move, $\mathcal{H}_{12}^0$ and $\mathcal{H}_{12}$, will be treated approximately in the following way: we shall expand this part of the Hamiltonian in terms of nuclear displacements. Two cases need to be considered: (i) initial state of the whole system at time t_0 and (ii) later times, $t > t_0$. In the former case nuclei from region 1 are displaced from their *equilibrium positions* $x^0 = \left(x_A^0\right)$, and $\mathcal{H}_{12}^0$ is expanded up to the second order in terms of them:

$$\mathcal{H}_{12}^0 \equiv \sum_{nm \in C} V_{nm}^0(x) c_n^\dagger c_m \tag{3}$$

where n, m are indices of the localized atomic basis placed on atoms in region 1 (this basis forms a set of orbitals C) to represent electrons, $c_n^\dagger$ and c_m are the corresponding electronic creation and annihilation operators in that region, while

$$V_{nm}^0(x) = \sum_A V_{nm}^{A,0} u_A + \frac{1}{2} \sum_{AB} V_{nm}^{AB,0} u_A u_B \tag{4}$$

are the corresponding matrix elements that depend on the nuclear displacements $u_A = x_A - x_A^0$. Note that the free term in the expansion, corresponding to zero displacements, is incorporated into the electrons-only Hamiltonian $\mathcal{H}_2^0$.

We need to have in mind that our goal here is to be able to study nuclear dynamics, and hence our nuclei may not simply oscillate, but follow a more complex trajectory at later times, $t > t_0$. To simplify the problem, in the spirit of CEID [109] we shall adopt a *harmonization approximation* [125] in which nuclear positions are assumed to deviate no more than quadratically from their "exact" instantaneous positions given by the mean nuclear trajectory $\langle x \rangle_t = (\langle x_A \rangle_t)$, where $\langle x_A \rangle_t = \mathrm{Tr}\left[\rho(t) x_A\right]$ and $\rho(t)$ is the density matrix of the combined system "electrons + nuclei":

$$\mathcal{H}_{12} \equiv \sum_{nm \in C} V_{nm} c_n^\dagger c_m \tag{5}$$

$$V_{nm} = \sum_A V_{nm}^A u_A + \frac{1}{2} \sum_{AB} V_{nm}^{AB} u_A u_B \tag{6}$$

where $u_A = x_A - \langle x_A \rangle_t$. Here the expansion coefficients V_{mn}^A and V_{mn}^{AB} will depend explicitly on the mean trajectory $\langle x \rangle_t$, and hence, on time t. Similarly to the equilibrium case, Eqs. (3) and (4), the free term in the expansion of $\mathcal{H}_{12}$ is incorporated into $\mathcal{H}_2$, so that the latter becomes implicitly time dependent via the dependence of V_{mn} on the mean trajectory, $\mathcal{H}_2 \equiv \mathcal{H}_2(t)$.

We stress here that the mean trajectory is not yet known, and our goal in this work is to derive an appropriate equation of motion for it. Since from the very beginning parameters of the Hamiltonian are assumed to depend on the mean trajectory, the equation of motion we are after may become non-linear, so that only numerical solution of these equations is anticipated.

2.2 Influence functional

We shall start by deriving an explicit expression for the nuclear density matrix, reduced with respect to the electronic subsystem and written in the nuclear coordinate representation by means of the path integrals method. The detailed derivation of all cases needed here is given in Appendix A.

As was shown in Ref. [123], the full propagator $\widehat{U}(t_1, t_0)$ of the whole combined system, written in the coordinate representation *with respect to the nuclear subsystem*, $\left\langle x_1 \left| \widehat{U}(t_1, t_0) \right| x_0 \right\rangle$, can be expressed via a path integral over nuclear trajectories:

$$\left\langle x_1 \left| \widehat{U}(t_1, t_0) \right| x_0 \right\rangle = \int_{x(t_0)=x_0}^{x(t_1)=x_1} \mathcal{D}x(t) e^{iS_1[x(t)]/\hbar} \widehat{U}_2(t_1, t_0) \tag{7}$$

where

$$\widehat{U}_2(t, t') = \widehat{\mathcal{T}}_+ \exp\left\{ -\frac{i}{\hbar} \int_{t'}^{t} [\mathcal{H}_2(t'') + \mathcal{H}_{12}(x(t''))] dt'' \right\} \tag{8}$$

is the electronic propagator (and hence the subscript 2), in which the trajectory $x(t)$ of nuclei enters as a "classical" *fixed* function (and hence serves as a parameter) via the coupling term, $\mathcal{H}_{12}$. The latter depends explicitly on time via its dependence on the trajectory $x(t)$ in the path integral, i.e. $\mathcal{H}_{12}$ is expanded as in Eqs. (5) and (6) with the displacements given by functions $u_A(t) = x_A(t) - \langle x_A \rangle_t$. Recall that $\mathcal{H}_2$ also depends on time, since nuclei are assumed to be clamped in their average positions $\langle x_A \rangle_t$ on the mean trajectory at each time t. The propagator satisfies usual equations of motion:

$$i\hbar \partial_t \widehat{U}_2(t, t') = [\mathcal{H}_2(t) + \mathcal{H}_{12}(x(t))] \widehat{U}_2(t, t')$$

$$-i\hbar \partial_{t'} \widehat{U}_2(t, t') = \widehat{U}_2(t, t') [\mathcal{H}_2(t') + \mathcal{H}_{12}(x(t'))] \tag{9}$$

Next, $S_1[x(t)]$ in Eq. (7) is the classical action associated with the isolated nuclear subsystem described by $\mathcal{H}_1$ only (which may depend on time). Finally, $\widehat{\mathcal{T}}$ is the time-ordering operator arranging operators in the exponent by their times ascending from right to left.

It is essential to stress, that the propagator (7) is an operator with respect to the electronic degrees of freedom, but is a classical object as far as the nuclei are concerned. This form is a hybrid between the Feynman (classical) and usual quantum (operator) representations of the propagator.

The evolution of the total density matrix $\widehat{\rho}(t_1)$ for the combined system (electrons + nuclei) is given by the corresponding solution of the Liouville equation,

$$\widehat{\rho}(t_1) = \widehat{U}(t_1, t_0) \widehat{\rho}(t_0) \widehat{U}(t_0, t_1) \tag{10}$$

which in the coordinate representation, again written with respect to the nuclei only, reads:

$$\langle x_1 | \rho(t_1) | x_0 \rangle = \int dx_2 dx_3 \left\langle x_1 \left| \widehat{U}(t_1, t_0) \right| x_2 \right\rangle \langle x_2 | \rho(t_0) | x_3 \rangle \left\langle x_3 \left| \widehat{U}(t_0, t_1) \right| x_0 \right\rangle$$

$$= \int dx_2 dx_3 \int_{x(t_0)=x_2}^{x(t_1)=x_1} \mathcal{D}x(t) \int_{x'(t_1)=x_0}^{x'(t_0)=x_3} \mathcal{D}x'(t) \, e^{i\left(S_1[x(t)] - S_1[x'(t)]\right)/\hbar} \widehat{U}_2(t_1, t_0) \langle x_2 | \rho(t_0) | x_3 \rangle \widehat{U}_2^\dagger(t_1, t_0) \tag{11}$$

Here the propagator $\widehat{U}_2(t_1, t_0)$ depends explicitly on the nuclear trajectories $x(t)$ taken forward in time between t_0 and t_1, while the propagator $\widehat{U}_2^\dagger(t_1, t_0) = \widehat{U}_2(t_0, t_1)$ depends explicitly on the nuclear trajectories $x'(t)$ taken backward in time, from t_1 to t_0. We shall explicitly indicate this by writing $\widehat{U}_2(t_1, t_0)_{x(t)}$ and $\widehat{U}_2(t_0, t_1)_{x'(t)}$ for the two propagators.

The matrix element $\langle x_2 | \widehat{\rho}(t_0) | x_3 \rangle$ of the initial density matrix is still an operator for electrons, and hence cannot be permuted with the two electronic propagators on both sides of it. However, assuming that the whole system was at thermal equilibrium at the initial time t_0,

$$\widehat{\rho}(t_0) = Z_0^{-1} e^{-\beta(\mathcal{H}_0 - \mu N)}, \quad Z_0 = \text{Tr}\left[e^{-\beta(\mathcal{H}_0 - \mu N)} \right] \tag{12}$$

where Z_0 is the partition function of the combined system at equilibrium at time t_0, $\beta = 1/k_B T$ is the inverse temperature, μ chemical potential and N number operator for the electrons. The $-\mu N$ term is convenient to absorb in the part $\mathcal{H}_2^0$ of the initial Hamiltonian $\mathcal{H}^0$, and this is what is implied in what follows. Since the initial density matrix is not assumed here as a direct product of the nuclear and electronic density matrices, our method is partition-less.

Using a similar argument as in Ref. [123], one can write the matrix element $\langle x_2 | \rho(t_0) | x_3 \rangle$ via an imaginary time path integral with respect to nuclei only (i.e. keeping it still as an operator in the electronic Hilbert space):

$$\langle x_2 | \widehat{\rho}(t_0) | x_3 \rangle = \frac{1}{Z_0} \int_{\overline{x}(0)=x_3}^{\overline{x}(\beta\hbar)=x_2} \mathcal{D}\overline{x}(\tau) \, e^{-S_1^0[\overline{x}(\tau)]/\hbar} \widehat{U}_2(\beta\hbar, 0) \tag{13}$$
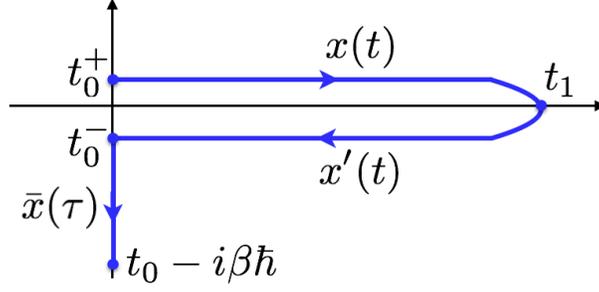
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Figure 1: Konstantinov-Perel's contour γ. On the horizontal upper (forward) track of the contour γ the coupling part of the Hamiltonian depends explicitly on the fixed nuclear trajectory $x(t)$, the horizontal lower (backward) track - on the fixed nuclear trajectory $x'(t)$, while the vertical track - on the fixed nuclear trajectory $\overline{x}(\tau)$ corresponding to Euclidean evolution.

Here $S_1^0[\overline{x}(\tau)]$ is the Euclidean action associated with the initial nuclear Hamiltonian $\mathcal{H}_1^0(x,p)$, and

$$\widehat{U}_2(\tau,\tau') = \overline{\mathcal{T}} \exp\left\{-\frac{1}{\hbar} \int_{\tau'}^{\tau} \left[\mathcal{H}_2^0 + \mathcal{H}_{12}(\overline{x}(\tau''))\right] d\tau''\right\} \tag{14}$$

is the Euclidean propagation operator and $\overline{\mathcal{T}}$ the imaginary time ordering operator. In particular, $\widehat{U}_2(\beta\hbar, 0)$ evolves the electronic subsystem in the imaginary time from $\tau' = 0$ to $\tau = \beta\hbar$. Here yet again the trajectory $\overline{x}(\tau)$ of nuclei (entering via the coupling term) is fixed, so that the propagation operator explicitly depends on it, to be indicated as $\widehat{U}_2(\beta\hbar, 0)_{\overline{x}(\tau)}$.

The operator (14) satisfies

$$-\hbar\partial_\tau \widehat{U}_2(\tau,\tau') = \left[\mathcal{H}_2^0 + \mathcal{H}_{12}(\overline{x}(\tau))\right] \widehat{U}_2(\tau,\tau')$$
$$\hbar\partial_{\tau'} \widehat{U}_2(\tau,\tau') = \widehat{U}_2(\tau,\tau') \left[\mathcal{H}_2^0 + \mathcal{H}_{12}(\overline{x}(\tau'))\right] \tag{15}$$

Using Eqs. (11) and (13), we can write for the density matrix of the combined system, still in the coordinate representation for nuclei, an expression:

$$\langle x_1 |\widehat{\rho}(t_1)| x_0\rangle = \frac{1}{Z_0} \int dx_2 dx_3 \int \mathcal{D}x(t) \int \mathcal{D}x'(t) \int \mathcal{D}\overline{x}(\tau) \, e^{\frac{i}{\hbar}\left(S_1[x(t)] - S_1[x'(t)]\right) - \frac{1}{\hbar}S_1^0[\overline{x}(\tau)]}$$

$$\times \widehat{U}_2(t_1, t_0)_{x(t)} \widehat{U}_2(\beta\hbar, 0)_{\overline{x}(\tau)} \widehat{U}_2^\dagger(t_1, t_0)_{x'(t)}$$

The obtained expression is still an operator for the electronic subsystem. To obtain the reduced density matrix for the nuclear subsystem we are interested in, we have to take a trace (to be denoted $\text{Tr}_2(\ldots)$) with respect to the Hilbert space associated with the electrons:

$$\langle x_1 |\widehat{\rho}_{ions}(t_1)| x_0\rangle = \frac{1}{Z_0} \int dx_2 dx_3 \int \mathcal{D}x(t) \int \mathcal{D}x'(t) \int \mathcal{D}\overline{x}(\tau) \, e^{\frac{i}{\hbar}\left(S_1[x(t)] - S_1[x'(t)]\right) - \frac{1}{\hbar}S_1^0[\overline{x}(\tau)]}$$

$$\times \text{Tr}_2\left[\widehat{U}_2(\beta\hbar, 0)_{\overline{x}(\tau)} \widehat{U}_2(t_0, t_1)_{x'(t)} \widehat{U}_2(t_1, t_0)_{x(t)}\right] \tag{16}$$

where the cyclic invariance of the trace has been used. This expression is not an operator anymore.

The product of the three operators under the trace, if read from right to left, has first a forward propagation from t_0 to t_1, then a backward propagation from t_1 to t_0, and, finally, imaginary time propagation from $t_0^- \equiv t_0 - i0$ to $t_0 - i\beta\hbar$. It is convenient to introduce a single contour consisting of these three parts: $t_0^+ \equiv t_0 + i0 \to t_1 \to t_0^- \to t_0 - i\beta\hbar$. This is known as the Konstantinov-Perel's contour, Fig. 1, which will be denoted hereafter as γ. It is essential that the time t_1 on γ is *fixed* as corresponding to the observation time (see the left hand side of Eq. (16)). Also, it is essential to remember that on each of the three parts (tracks) of the contour the coupling Hamiltonian $\mathcal{H}_{12}$ is taken with a particular fixed nuclear trajectory, either $x(t)$, or $x'(t)$ on the horizontal tracks, and $\mathcal{H}_{12}^0$ with $\overline{x}(\tau)$ on the vertical one. This brings a time dependence to the electronic problem; it is additional to any other existing, e.g. due to the time dependent field and the harmonisation approximation.

Hence, denoting the product as a single operator,

$$\widehat{U}_\gamma(t_0 - i\beta\hbar, t_0^+) = \widehat{U}_2(\beta\hbar, 0)_{\overline{x}(\tau)} \widehat{U}_2(t_0, t_1)_{x'(t)} \widehat{U}_2(t_1, t_0)_{x(t)} \tag{17}$$

and using the fact that the order in which the operators appear in the product is fixed, it is possible to rewrite it as a single evolution operator over the whole contour:

$$\widehat{U}_\gamma \left(t_0 - i\beta\hbar, t_0^+\right) = \widehat{\mathcal{T}}_\gamma \exp\left\{-\frac{i}{\hbar}\int_\gamma H_2\left(z_1\right)dz_1\right\} \tag{18}$$

Here $\widehat{\mathcal{T}}_\gamma$ is the time ordering operator on the contour with the direction of $z_1 \in \gamma$ increasing as shown by arrows in Fig. 1. The integral over the contour consists of a sum of three integrals: over the upper, then lower and finally over the vertical tracks with the electronic Hamiltonian in each part of the contour (written by the corresponding Roman letter) defined as follows:

$$H_2(z) \equiv \begin{cases} \mathcal{H}_2(t) + \mathcal{H}_{12}\left(x(t)\right) & \text{if } z \in \text{upper track} \\ \mathcal{H}_2(t) + \mathcal{H}_{12}\left(x'(t)\right) & \text{if } z \in \text{lower track} \\ \mathcal{H}_2^0 + \mathcal{H}_{12}^0\left(\overline{x}(t)\right) & \text{if } z \in \text{vertical track} \end{cases} \tag{19}$$

We have explicitly indicated here how the electron-nuclear part depends on the nuclear positions on each track. The electron-nuclear part of the Hamiltonian, $\mathcal{H}_{12}$ and $\mathcal{H}_{12}^0$, are given by Eqs. (3)-(6), where atomic displacements u_A are given somewhat differently depending on the track on the contour γ: on the horizontal tracks the "classical" displacement of the degree of freedom A is defined as $u_A(t) = x_A(t) - \langle x_A \rangle_t$ (upper) and $u'_A(t) = x'_A(t) - \langle x_A \rangle_t$ (lower), while on the vertical track the displacement $\overline{u}_A(\tau) = x_A(\tau) - x_A^0$ is used that is defined with respect to the equilibrium positions of the atoms. The matrices $\mathbf{V}^A(z) = \left(V_{nm}^A(z)\right)$ and $\mathbf{V}^{AB}(z) = \left(V_{nm}^{AB}(z)\right)$, see Eqs. (4) and (6), may still depend on $z \in \gamma$ on the horizontal tracks via its possible dependence on the averages $\langle x_A \rangle_t$, i.e. they are $\mathbf{V}^A(t)$ and $\mathbf{V}^{AB}(t)$ on both tracks, while on the vertical track there is no time dependence, i.e. $\mathbf{V}^A(\tau) \equiv \mathbf{V}_0^A$ and $\mathbf{V}^{AB}(\tau) \equiv \mathbf{V}_0^{AB}$, the values at thermal equilibrium.

In all these cases the nuclear trajectories are fixed (by the corresponding path integrals in Eq. (16)), i.e. they serve as "external" parameters (functions). As will be clear later on, the fact that the Hamiltonian on each track is different and depends on time in this rather general way creates additional complications in developing theory.

For the following it is convenient to introduce a more general evolution operator between any two variables z and z' somewhere on γ,

$$\widehat{U}_\gamma\left(z, z'\right) = \widehat{\mathcal{T}}_\gamma \exp\left\{-\frac{i}{\hbar}\int_{z'}^z H_2\left(z_1\right)dz_1\right\} \tag{20}$$

The operator (18) is obtained by taking $z = t_0 - i\beta\hbar$ and $z' = t_0^+$, and the electronic Hamiltonian $H_2(z)$ on γ is defined as described above. By its definition (20), $\widehat{U}_\gamma\left(z, z'\right)$ is essentially a product of the required number of evolution operators, which are necessary to bridge the two "times" z and z'. Hence, using Eqs. (9) and (15) and the fact that on the imaginary (vertical) track $z = t_0 - i\tau$, the propagator $\widehat{U}_\gamma\left(z, z'\right)$ is seen to satisfy the usual equations of motion:

$$i\hbar\partial_z\widehat{U}_\gamma\left(z, z'\right) = H_2(z)\widehat{U}_\gamma\left(z, z'\right)$$
$$-i\hbar\partial_{z'}\widehat{U}_\gamma\left(z, z'\right) = \widehat{U}_\gamma\left(z, z'\right)H_2\left(z'\right) \tag{21}$$

Concluding, the trace of the product of three electronic propagators can be written as

$$\text{Tr}_2\left[\widehat{U}_2\left(\beta\hbar, 0\right)_{\overline{x}(\tau)} \widehat{U}_2\left(t_0, t_1\right)_{x'(t)} \widehat{U}_2\left(t_1, t_0\right)_{x(t)}\right] = \text{Tr}_2\left[\widehat{U}_\gamma\left(t_0 - i\beta\hbar, t_0^+\right)\right] \equiv \left\langle\widehat{U}_\gamma\left(t_0 - i\beta\hbar, t_0^+\right)\right\rangle_2 \tag{22}$$

and hence we have to develop methods of calculating the trace of the electronic propagation operator in the right hand side.

Following the steps of Ref. [123], one can derive a useful formula for the required expectation value $\left\langle\widehat{U}_\gamma\left(t_0 - i\beta\hbar, t_0^+\right)\right\rangle_2$ of the evolution operator (18) on γ that would enable us to define the (generalised) electronic Green's function later on. We first introduce a parameter λ that stipulates the strength of the coupling term:

$$H_2^\lambda(z) \equiv \begin{cases} \mathcal{H}_2(t) + \lambda\mathcal{H}_{12}\left(x(t)\right) & \text{if } z \in \text{upper track} \\ \mathcal{H}_2(t) + \lambda\mathcal{H}_{12}\left(x'(t)\right) & \text{if } z \in \text{lower track} \\ \mathcal{H}_2^0 + \lambda\mathcal{H}_{12}\left(\overline{x}(t)\right) & \text{if } z \in \text{vertical track} \end{cases} \tag{23}$$

Here, $H_2^\lambda(z)$ is defined with either $x(t)$, $x'(t)$ or $\overline{x}(\tau)$, depending on the position of the variable z on the contour γ. At $\lambda = 1$ we have our original Hamiltonian (19). At $\lambda = 0$ the electron-ion coupling is completely switched off, although electrons still interact (via $\mathcal{H}_2$ or $\mathcal{H}_2^0$) with nuclei clamped at their respective positions. Correspondingly,

in $\mathcal{H}_2$ nuclei are assumed to be at positions $\langle x_A \rangle_t$ for z anywhere on the horizontal tracks, while on the vertical track they are at equilibrium positions x_A^0.

Next, we define a new evolution operator via

$$\widehat{U}_\gamma^\lambda (z, z') = \widehat{\mathcal{T}}_\gamma \exp \left\{ -\frac{i}{\hbar} \int_{z'}^z H_2^\lambda (z_1) \, dz_1 \right\} \tag{24}$$

between any two points z and z' on γ. At $\lambda = 1$ this operator goes over into the one we introduced above, Eq. (20), and which we actually need. The new operator satisfies the usual equations of motion:

$$i\hbar \partial_z \widehat{U}_\gamma^\lambda (z, z') = H_2^\lambda(z) \widehat{U}_\gamma^\lambda (z, z')$$

$$-i\hbar \partial_{z'} \widehat{U}_\gamma^\lambda (z, z') = \widehat{U}_\gamma^\lambda (z, z') H_2^\lambda (z') \tag{25}$$

Then, it follows from a well-known expression valid on the contour γ that

$$\frac{\partial}{\partial \lambda} \widehat{U}_\gamma^\lambda (z, z') = -\frac{i}{\hbar} \int_\gamma dz_1 \widehat{U}_\gamma^\lambda (z, z_1) \frac{\partial H_2^\lambda (z_1)}{\partial \lambda} \widehat{U}_\gamma^\lambda (z_1, z') = -\frac{i}{\hbar} \int_\gamma dz_1 \widehat{U}_\gamma^\lambda (z, z_1) \mathcal{H}_{12} (z_1) \widehat{U}_\gamma^\lambda (z_1, z') \tag{26}$$

Therefore, the derivative of the trace of the evolution operator with the times on γ as appearing in Eq. (22) can be written as

$$\frac{\partial}{\partial \lambda} \left\langle \widehat{U}_\gamma^\lambda \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2 = -\frac{i}{\hbar} \int_\gamma dz_1 \left\langle \widehat{U}_\gamma^\lambda (t_0 - i\beta\hbar, z_1) \mathcal{H}_{12} (z_1) \widehat{U}_\gamma^\lambda (z_1, t_0^+) \right\rangle_2$$

Dividing both sides of this equation by $\left\langle \widehat{U}_\gamma^\lambda \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2$ and integrating with respect to λ between 0 and 1, one obtains:

$$\left\langle \widehat{U}_\gamma \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2 \equiv \left\langle \widehat{U}_\gamma^\lambda \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2^{\lambda=1} = Z_2^0 \exp \left\{ \frac{i}{\hbar} \Delta S_{eff} [x(t), x'(t), \overline{x}(\tau)] \right\} \tag{27}$$

where we have introduced an effective action

$$\Delta S_{eff} [x(t), x'(t), \overline{x}(\tau)] = -\int_0^1 d\lambda \int_\gamma dz_1 \, \mathcal{F}_\lambda (z_1) \tag{28}$$

where

$$\mathcal{F}_\lambda(z) = \frac{\left\langle \widehat{U}_\gamma^\lambda (t_0 - i\beta\hbar, z) \mathcal{H}_{12} (z) \widehat{U}_\gamma^\lambda \left(z, t_0^+ \right) \right\rangle_2}{\left\langle \widehat{U}_\gamma^\lambda \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2} \tag{29}$$

In deriving the above result, use has been made of the fact that at $\lambda = 0$ the coupling between the nuclei and electrons disappears, and hence

$$\left\langle \widehat{U}_\gamma^\lambda \left(t_0 - i\beta\hbar, t_0^+ \right) \right\rangle_2^{\lambda=0} = \text{Tr} \left[\widehat{U}_2 \left(t_0 - i\beta\hbar, t_0^- \right) \widehat{U}_2 \left(t_0^-, t_1 \right) \widehat{U}_2 \left(t_1, t_0^+ \right) \right]_{\lambda=0}$$

$$= \text{Tr} \left[\widehat{U}_2 \left(t_0 - i\beta\hbar, t_0^- \right) \right] = \text{Tr} \left[e^{-\beta \mathcal{H}_2^0} \right] = Z_2^0$$

is the electron-only partition function at t_0 calculated while nuclei are clamped at their equilibrium positions $x^0 = \left(x_A^0 \right)$.

Hence, finally, we obtain for the reduced density matrix of nuclei an expression:

$$\langle x_1 | \widehat{\rho}_{ions} (t_1) | x_0 \rangle = \frac{Z_2^0}{Z_0} \int dx_2 dx_3 \int \mathcal{D}x(t) \int \mathcal{D}x'(t) \int \mathcal{D}\overline{x}(\tau) \, e^{\frac{i}{\hbar} \left(S_1 - S_1' + \Delta S_{eff} \right) - \frac{1}{\hbar} S_1^0} \tag{30}$$

where $S_1 \equiv S_1 [x(t)]$, $S_1' \equiv S_1 [x'(t)]$, $S_1^0 \equiv S_1^0 [\overline{x}(\tau)]$ and ΔS_{eff} depends on all three trajectories. The pre-factor Z_2^0 / Z_0 is a constant, which depends on temperature. We will have to consider it later on.

The above expression contains all the information about the electronic subsystem in the form of the influence functional, i.e. in the expression in the exponent, which is basically the effective action ΔS_{eff}. The obtained result generalizes the formula obtained in Refs. [123, 45] for the partitioned case to the one in which the electrons and nuclei are considered coupled from the very beginning, i.e. at initial thermalization. Hence, our method is strictly partition-less, and hence, at least in principle, consideration of a response of the system in real time to external time-dependent perturbations should be possible (e.g. bias switch on).

2.3 Green's function

Because the Hamiltonian $H_2^\lambda(z)$ is different on both horizontal tracks of γ, the two possible positions of the initial time t_0, either on the upper (as t_0^+) or lower (t_0^-) tracks, are not equivalent. Hence, the definition of the Heisenberg picture is not unique. Therefore, the electronic Green's function (GF) cannot be introduced in the usual way via the operators in the Heisenberg representation as this appears to be ambiguous. Following Ref. [126], we generalize the definition of the GF as follows:

$$G_{ab}^\lambda(z, z') = -\frac{i}{Z^\lambda \hbar} \begin{cases} \left\langle \widehat{U}_\gamma^\lambda(t_0 - i\beta\hbar, z) c_a \widehat{U}_\gamma^\lambda(z, z') c_b^\dagger \widehat{U}_\gamma^\lambda(z', t_0^+) \right\rangle_2 & \text{if } z > z' \\ -\left\langle \widehat{U}_\gamma^\lambda(t_0 - i\beta\hbar, z') c_b^\dagger \widehat{U}_\gamma^\lambda(z', z) c_a \widehat{U}_\gamma^\lambda(z, t_0^+) \right\rangle_2 & \text{if } z < z' \end{cases} \tag{31}$$

where

$$Z^\lambda = \left\langle \widehat{U}_\gamma^\lambda(t_0 - i\beta\hbar, t_0^+) \right\rangle_2 \tag{32}$$

and the arguments z and z' in the GF could be anywhere on the contour γ. Here, and in the following, the indices like a, b correspond to any atomic orbital in the whole electronic system, either included in the set C or not. We shall use indices like n, m to indicate orbitals from region C only. Note that the usual definition of the GF can also be brought into the form above where the two propagation operators between c_a and $c_b^\dagger$ are combined into one; hence, the defined above GF satisfies usual equations of motion.

Note in passing an important point, which shall be used extensively in the following, that it is e.g. insufficient to indicate whether the GF is "lesser" or "greater" as it may also be necessary to indicate explicitly on which tracks of γ the two "time" variables actually are. This will be indicated explicitly by the indices $+$, $-$ or M depending on whether each variable is on the upper, lower or vertical track. For instance, if both variables $z, z' \in +$, then we shall us the notation $\mathbf{G}_{++}(z, z')$, and then one can also introduce a lesser, greater, retarded and advanced components; if $z \in +$ and $z' \in M$, then we shall use $\mathbf{G}_{+M}(z, z')$ (which is a lesser component) as the usual notation $\mathbf{G}^\rceil(z, z')$ is insufficient as it is still not clear on which horizontal track the variable z lies. Only for GFs defined in such a way that the same Hamiltonian is used on both horizontal tracks, usual notations (without $+$ and $-$) are applicable.

With this definition, the function $\mathcal{F}_\lambda(z)$ in Eq. (29), needed for calculating the effective action, Eq. (28), becomes:

$$\mathcal{F}_\lambda(z) = -i\hbar \sum_{nm \in C} V_{nm}(x(z)) G_{mn}^\lambda(z, z^+) = -i\hbar \operatorname{tr}_C \left\{ \mathbf{V}(x(z)) \mathbf{G}^\lambda(z, z^+) \right\} \tag{33}$$

where the trace written above using small letters corresponds to the usual trace of a matrix; $\mathbf{V}$ and $\mathbf{G}$ are the matrices composed of the matrix elements V_{nm} of the electron-nuclear coupling and G_{mn} of the GF. Hence, the effective action reads

$$\Delta S_{eff}[x(t), x'(t), \overline{x}(\tau)] = i\hbar \int_0^1 d\lambda \int_\gamma dz \operatorname{tr}_C \left\{ \mathbf{V}(x(z)) \mathbf{G}^\lambda(z, z^+) \right\} \equiv i\hbar \int_0^1 d\lambda \int_\gamma dz \operatorname{tr}_C \left\{ \mathbf{V}(x(z)) \mathbf{G}^{\lambda, <}(z, z) \right\} \tag{34}$$

In the last two equations z^+ is infinitesimally "later" on the contour γ than z, so that essentially only the lesser GF is needed on the contour (the last equality). This formula is analogous to the one derived initially in Ref. [45, 126] based on the partitioned approach; as we shall see, going beyond this approximation simply extends the integration from Keldysh to Konstantinov-Perel contour.

Writing the contour integral in Eq. (34) explicitly, we obtain for the effective action:

$$\Delta S_{eff}[x(t), x'(t), \overline{x}(\tau)]$$

$$= i\hbar \int_0^1 d\lambda \left\{ \int_{t_0}^{t_1} dt \operatorname{tr}_C \left[\mathbf{V}_+(t) \mathbf{G}_{++}^{\lambda, <}(t, t) - \mathbf{V}_-(t) \mathbf{G}_{--}^{\lambda, <}(t, t) \right] - i \int_0^{\beta\hbar} d\tau \operatorname{tr}_C \left[\mathbf{V}_M(\tau) \mathbf{G}_{MM}^{\lambda, <}(\tau, \tau) \right] \right\} \tag{35}$$

The electronic GF introduced above depends explicitly on the strength parameter λ. At $\lambda = 0$, no electron-nuclear interaction exists and nuclei are assumed to be clamped at either positions $\langle x_A \rangle_t$ or x_A^0, as explained above. The GF, corresponding to the absence of interaction between electrons and nuclear displacements, will be denoted $\mathbb{G}(z, z') = (\mathbb{G}_{ab}(z, z'))$. This GF corresponds to the Hamiltonian $H_2^{\lambda=0}$, Eq. (23), where electron-nuclear interaction is included only in the zeroth order with nuclei following the mean trajectory $\langle x \rangle_t$ on both horizontal tracks and placed at equilibrium x^0 on the vertical track. Correspondingly, the Hamiltonian on the horizontal tracks is the same for $\mathbb{G}$ (and the usual Langreth rules [122] apply) and hence this particular GF is exactly the same as the usual one; there is no need to indicate explicitly on which tracks the times are, one can use lesser, greater, etc. (usual) notations for $\mathbb{G}$ without confusion.

The interactions of electrons with nuclear displacements, Eqs. (3) and (5), is a one-particle operator

$$\lambda \mathcal{H}_{12}(z) = \lambda \sum_{nm \in C} V_{nm}(z) c_n^\dagger c_m$$

(and similarly for $\mathcal{H}_{12}^0$), and hence the two GF, $\mathbb{G}$ and $\mathbf{G}^\lambda$, are related via the Dyson equation:

$$\mathbf{G}^\lambda(z, z') - \mathbb{G}(z, z') = \lambda \int_\gamma dz_1 \, \mathbb{G}(z, z_1) \mathbf{V}(z_1) \mathbf{G}^\lambda(z_1, z') = \lambda \int_\gamma dz_1 \, \mathbf{G}^\lambda(z, z_1) \mathbf{V}(z_1) \mathbb{G}(z_1, z') \qquad (36)$$

Note that in the following only this equation will be explored. Since it is valid for any electronic Hamiltonian that may even include electronic correlations, the method to be adopted below is general; we shall assume, however, that the calculation of the unperturbed GF $\mathbb{G}(z, z')$ is feasible. Note that this equation is also valid for the CC block of the GF, $\mathbf{G}_{CC}^\lambda(z, z')$, in the situation when only within region C nuclei are allowed to move (see Appendix B); in this case the vector function $\mathbf{V}(z) \to \mathbf{V}_C(z)$ is defined only on this region's orbitals ($V_{ab} \neq 0$ only if the orbitals $a, b \in C$).

Further, we note that since the matrices $\mathbf{V}_\pm(t)$ and $\mathbf{V}_M(\tau)$ are non-zero only within region C, only CC elements of the GF are needed in Eq. (35) to calculate the effective action (the influence functional). This also means that only CC elements of the unperturbed GF $\mathbb{G}(z, z')$ are needed in the Dyson equation. If the set C does not cover the whole system, e.g. it corresponds only to the central region (molecule) in the quantum transport setup, then calculation of the contribution due to other orbitals (of the leads in the case of the quantum transport) is required. If the interaction between orbitals in C and the rest of the system is described in the one-electron approximation, then the contribution to the CC block, $\mathbb{G}_{CC}(z, z')$, from the rest of the system appears in the usual way via a self-energy (Appendix B).

Hence, the calculation of the action, Eq. (35), requires three lesser components of the total electronic Green's function with the coupling added using the strength λ. This requires solving the Dyson equation (36). We shall do it approximately by noting that the atomic displacements $u_A(t)$, $u_A'(t)$ and $\bar{u}_A(\tau)$, with respect to which the paths integrals are actually calculated in Eq. (30), enter here only via the matrix $\mathbf{V}(z) = (V_{nm}(x(z)))$. We shall expand the GF in powers of this matrix reiterating the Dyson equation. Since the effective action (34) is already proportional to such a matrix, and a progress can only be made if the effective action is quadratic with respect to atomic displacements, we shall limit ourselves with the first order term only (cf. [45]):

$$\mathbf{G}^\lambda(z, z') \simeq \mathbb{G}(z, z') + \lambda \int_\gamma dz_1 \mathbb{G}(z, z_1) \mathbf{V}(z_1) \mathbb{G}(z_1, z') \qquad (37)$$

We stress, that this approximation does not imply that the electron-nuclear coupling is small; rather, we treat nuclear displacements from the corresponding mean positions (either $\langle x_A \rangle_t$ or x_A^0 on the horizontal and vertical tracks, respectively) as small. Calculation of the contour integral in the above equation requires an appropriate generalization of the Langreth rules which the reader can find in Appendix C.

We now have everything we need to calculate the effective action.

2.4 Calculation of the effective action

Using the generalised Langreth rules in Eq. (37), one can calculate all three components of the lesser GF required in Eq. (35): on the upper track,

$$\mathbf{G}_{++}^{\lambda <}(t, t) \simeq \mathbb{G}^<(t, t) - i\lambda \int_0^{\beta\hbar} d\tau \, \mathbb{G}^\rceil(t, \tau) \mathbf{V}_M(\tau) \mathbb{G}^\lceil(\tau, t) + \lambda \int_{t_0}^{t_1} dt' \, \big[\mathbb{G}^r(t, t') \mathbf{V}_+(t') \mathbb{G}^<(t', t)$$

$$+ \mathbb{G}^<(t, t') \mathbf{V}_+(t') \mathbb{G}^a(t', t) + \mathbb{G}^<(t, t') (\mathbf{V}_+(t') - \mathbf{V}_-(t')) \mathbb{G}^>(t', t) \big] \qquad (38)$$

on the lower track,

$$\mathbf{G}_{--}^{\lambda <}(t, t) \simeq \mathbb{G}^<(t, t) - i\lambda \int_0^{\beta\hbar} d\tau \, \mathbb{G}^\rceil(t, \tau) \mathbf{V}_M(\tau) \mathbb{G}^\lceil(\tau, t) + \lambda \int_{t_0}^{t_1} dt' \, \big[\mathbb{G}^r(t, t') \mathbf{V}_-(t') \mathbb{G}^<(t', t) \qquad (39)$$

$$+ \mathbb{G}^<(t, t') \mathbf{V}_-(t') \mathbb{G}^a(t', t) + \mathbb{G}^>(t, t') (\mathbf{V}_+(t') - \mathbf{V}_-(t')) \mathbb{G}^<(t', t) \big]$$

and on the vertical track,

$$\mathbf{G}_{MM}^{\lambda <}(\tau, \tau) \simeq \mathbb{G}_{MM}^<(\tau, \tau) - i\lambda \int_0^{\beta\hbar} d\tau' \, \big[\mathbb{G}_{MM}^r(\tau, \tau') \mathbf{V}_M(\tau') \mathbb{G}_{MM}^<(\tau', \tau)$$

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$$+\mathbb{G}_{MM}^{<}\left(\tau,\tau'\right)\mathbf{V}_M\left(\tau'\right)\mathbb{G}_{MM}^{a}\left(\tau',\tau\right)+\mathbb{G}_{MM}^{<}\left(\tau,\tau'\right)\mathbf{V}_M\left(\tau'\right)\mathbb{G}_{MM}^{>}\left(\tau',\tau\right)]$$

$$+\lambda\int_{t_0}^{t_1}dt\,\mathbb{G}^{\lceil}\left(\tau,t\right)\left(\mathbf{V}_+\left(t\right)-\mathbf{V}_-\left(t\right)\right)\mathbb{G}^{\rceil}\left(t,\tau\right) \tag{40}$$

Here, the dependence of the GF components on the coupling strength is shown explicitly. As was already indicated, the unperturbed (electron-only, i.e. without the coupling) GF $\mathbb{G}$ is defined for the Hamiltonian which is the same on both horizontal tracks. Therefore, there is no need to indicate the particular track anymore, and hence the $+/-$ subscripts have been omitted. Also, the right and left functions like $\mathbb{G}_{+M}$ or $\mathbb{G}_{M-}$, which have one time on the vertical and one on the horizontal tracks, do not require indicating explicitly which horizontal track is used, and hence can simply be denoted as $\mathbb{G}^{\rceil}$ and $\mathbb{G}^{\lceil}$, respectively.

The first (λ independent) term in the above expansions for the three components of the GF gives rise to the first order approximation to the effective action, Eq. (35):

$$\Delta S_{eff}^{(1)}[u(t),u'(t),\overline{u}(\tau)]=i\hbar\,\mathrm{tr}_C\left\{\int_{t_0}^{t_1}dt\left[\mathbf{V}_+(t)-\mathbf{V}_-(t)\right]\mathbb{G}^{<}\left(t,t\right)-i\int_0^{\beta\hbar}d\tau\,\mathbf{V}_M\left(\tau\right)\mathbb{G}_{MM}^{<}\left(\tau,\tau\right)\right\} \tag{41}$$

Using Eqs. (4) and (6) to express the electron-nuclear matrix elements on different parts of γ via atomic displacements, we obtain:

$$\Delta S_{eff}^{(1)}[u(t),u'(t),\overline{u}(\tau)]=\int_{t_0}^{t_1}dt\left[\sum_A i\hbar Y_A^{<}\left(t\right)\left(u_A(t)-u'_A(t)\right)+\frac{i\hbar}{2}\sum_{AB}Y_{AB}^{<}(t)\left(u_A(t)u_B(t)-u'_A(t)u'_B(t)\right)\right]$$

$$+\int_0^{\beta\hbar}d\tau\left[\sum_A\hbar\overline{Y}_A^{<}\left(\tau\right)\overline{u}_A\left(\tau\right)+\frac{\hbar}{2}\sum_{AB}\overline{Y}_{AB}^{<}\left(\tau\right)\overline{u}_A\left(\tau\right)\overline{u}_B\left(\tau\right)\right] \tag{42}$$

where

$$Y_A^{<}\left(t\right)=\mathrm{tr}_C\left[\mathbb{G}^{<}\left(t,t\right)\mathbf{V}^A\left(t\right)\right] \tag{43}$$

$$Y_{AB}^{<}\left(t\right)=\mathrm{tr}_C\left[\mathbb{G}^{<}\left(t,t\right)\mathbf{V}^{AB}\left(t\right)\right] \tag{44}$$

$$\overline{Y}_A^{<}\left(\tau\right)=\mathrm{tr}_C\left[\mathbb{G}_{MM}^{<}\left(\tau,\tau\right)\mathbf{V}_0^A\right] \tag{45}$$

$$\overline{Y}_{AB}^{<}\left(\tau\right)=\mathrm{tr}_C\left[\mathbb{G}_{MM}^{<}\left(\tau,\tau\right)\mathbf{V}_0^{AB}\right] \tag{46}$$

Hence, the first order effective action contains both linear and quadratic terms with respect to atomic displacements. Above, scalar functions of real and imaginary times, Eqs. (43)-(46), have been defined.

Consider now the second order term which is obtained from the other terms in Eqs. (38), (39) and (40), that are proportional to λ. Note that as the arguments of the functions in the terms appearing in convolutions are implicit, there is no need anymore to show them explicitly. We obtain after some algebra:

$$\Delta S_{eff}^{(2)}[u(t),u'(t),\overline{u}(\tau)]=-\frac{i\hbar}{2}\int_0^{\beta\hbar}d\tau\int_0^{\beta\hbar}d\tau'\,\mathrm{tr}_C\left\{\mathbf{V}_M\mathbb{G}_{MM}^{<}\mathbf{V}_M\left(\mathbb{G}_{MM}^{r}+\mathbb{G}_{MM}^{a}+\mathbb{G}_{MM}^{>}\right)\right\}$$

$$+\frac{i\hbar}{2}\int_{t_0}^{t_1}dt\int_{t_0}^{t_1}dt'\,\mathrm{tr}_C\left[\left(\mathbb{G}^r+\mathbb{G}^a\right)\left(\mathbf{V}_+\mathbb{G}^{<}\mathbf{V}_+-\mathbf{V}_-\mathbb{G}^{<}\mathbf{V}_-\right)+\left(\mathbf{V}_+-\mathbf{V}_-\right)\left(\mathbb{G}^{>}\mathbf{V}_+\mathbb{G}^{<}-\mathbb{G}^{<}\mathbf{V}_-\mathbb{G}^{>}\right)\right]$$

$$+\hbar\int_0^{\beta\hbar}d\tau\int_{t_0}^{t_1}dt\,\mathrm{tr}_C\left[\left(\mathbf{V}_+-\mathbf{V}_-\right)\mathbb{G}^{\rceil}\mathbf{V}_M\mathbb{G}^{\lceil}\right] \tag{47}$$

The transformations that follow are simple but rather cumbersome. We first introduce new functions on the horizontal tracks,

$$v_A(t)=u_A(t)-u'_A(t)\text{ and }r_A(t)=\frac{1}{2}\left[u_A(t)+u'_A(t)\right] \tag{48}$$

in terms of which the first and the second order contributions to the action read:

$$\Delta S_{eff}[u(t),u'(t),\overline{u}(\tau)]=i\hbar\int_{t_0}^{t_1}dt\sum_A Y_A^{<}\left(t\right)v_A(t)+\hbar\int_0^{\beta\hbar}d\tau\sum_A\overline{Y}_A^{<}\left(\tau\right)\overline{u}_A\left(\tau\right)$$

$$+\frac{i\hbar}{2} \int_{t_0}^{t_1} dt \int_{t_0}^{t_1} dt' \sum_{AB} \left\{ L_{AB}\left(t, t'\right) v_A\left(t\right) v_B\left(t'\right) + K_{AB}\left(t, t'\right) r_A\left(t\right) v_B\left(t'\right) \right\}$$

$$+\hbar \int_0^{\beta\hbar} d\tau \int_{t_0}^{t_1} dt \sum_{AB} Y_{AB}^{\rceil\lceil}\left(\tau, t\right) \overline{u}_A(\tau) v_B(t) - \frac{i\hbar}{2} \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \sum_{AB} \overline{L}_{AB}\left(\tau, \tau'\right) \overline{u}_A\left(\tau\right) \overline{u}_B\left(\tau'\right) \tag{49}$$

where the following scalar functions were introduced:

$$L_{AB}\left(t, t'\right) = \frac{1}{2} \left[Y_{BA}^{><}\left(t, t'\right) + Y_{BA}^{<>}\left(t, t'\right) \right] \equiv L_{BA}\left(t', t\right) \tag{50}$$

$$K_{AB}\left(t, t'\right) = 2\delta\left(t - t'\right) Y_{AB}^{<}(t) - 2\theta_{t't} \left[Y_{BA}^{><}\left(t, t'\right) - Y_{BA}^{<>}\left(t, t'\right) \right] \tag{51}$$

$$\overline{L}_{AB}\left(\tau, \tau'\right) = i\delta\left(\tau - \tau'\right) \overline{Y}_{AB}^{<}\left(\tau\right) + \theta_{\tau\tau'} \overline{Y}_{BA}^{<>}\left(\tau, \tau'\right) + \theta_{\tau'\tau} \overline{Y}_{BA}^{><}\left(\tau, \tau'\right) \equiv \overline{L}_{BA}\left(\tau', \tau\right) \tag{52}$$

where $\theta_{tt'}$ $\left(\theta_{\tau\tau'}\right)$ is the Heaviside function on the upper (vertical) track of the contour. Note that the objects $L_{AB}\left(t, t'\right)$ and $\overline{L}_{AB}\left(\tau, \tau'\right)$ form symmetric matrices. Several Y and $\overline{Y}$ double time functions have also been defined:

$$Y_{AB}^{\alpha\beta}\left(t, t'\right) = \mathrm{tr}_C \left\{ \mathbb{G}^\alpha\left(t, t'\right) \mathbf{V}^A\left(t'\right) \mathbb{G}^\beta\left(t', t\right) \mathbf{V}^B\left(t\right) \right\} \tag{53}$$

$$\overline{Y}_{AB}^{\alpha\beta}\left(\tau, \tau'\right) = \mathrm{tr}_C \left\{ \mathbb{G}_{MM}^\alpha\left(\tau, \tau'\right) \mathbf{V}_0^A \mathbb{G}_{MM}^\beta\left(\tau', \tau\right) \mathbf{V}_0^B \right\} \tag{54}$$

$$Y_{AB}^{\rceil\lceil}\left(\tau, t\right) = \mathrm{tr}_C \left\{ \mathbb{G}^{\rceil}\left(t, \tau\right) \mathbf{V}_0^A \mathbb{G}^{\lceil}\left(\tau, t\right) \mathbf{V}^B\left(t\right) \right\} \tag{55}$$

where α, β indicate various components $<, >$ of the GFs contained in the trace. In simplifying the above expression use have been made of the identities relating the retarded and advanced GFs with the greater and lesser ones, $\mathbb{G}^r\left(z, z'\right) = \theta_{zz'}\left(\mathbb{G}^>\left(z, z'\right) - \mathbb{G}^<\left(z, z'\right)\right)$ and $\mathbb{G}^a\left(z, z'\right) = -\theta_{z'z}\left(\mathbb{G}^>\left(z, z'\right) - \mathbb{G}^<\left(z, z'\right)\right)$ which are valid when both arguments belong either to the horizontal or vertical tracks of γ.

Concluding, we have got an expression for the effective action which is found to be a second order form with respect to the functions $v_A(t)$, $r_A(t)$ and $\overline{u}_A\left(\tau\right)$. When inserting the effective action into the matrix element of the reduced density matrix, Eq. (30), linear terms in displacements can easily be incorporated into the existing actions as they contain single time integrals; however, this is not the case for quadratic in displacement terms as they enter via double time integrals. Therefore, a procedure is required to linearilize them.

2.5   Real-imaginary time Hubbard-Stratonovich transformation

Consider two sets of functions, $\left\{k_i^A(t)\right\}$ and $\left\{\overline{k}_j^A(\tau)\right\}$, defined for real and imaginary times, respectively, and the corresponding complex Gaussian noises $\left\{z_i^A(t)\right\}$ and $\left\{\overline{z}_i^A(\tau)\right\}$. A different number of functions may be in each set. Then, the following identity can be established [127] (see also [128] where the same identity was written via contour integrals):

$$\left\langle \exp\left\{ i\sum_A \left[\int_{t_0}^{t_1} dt \sum_i z_i^A(t) k_i^A(t) + \int_0^{\beta\hbar} d\tau \sum_j \overline{z}_j^A\left(\tau\right) \overline{k}_j^A\left(\tau\right) \right] \right\} \right\rangle_{\{z, \overline{z}\}}$$

$$= \exp\left\{ -\frac{1}{2} \sum_{AB} \left[\int_{t_0}^{t_1} dt \int_{t_0}^{t_1} dt' \sum_{ii'} k_i^A(t) k_{i'}^B\left(t'\right) \Pi_{ii'}^{AB}\left(t, t'\right) + \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \sum_{jj'} \overline{k}_j^A(\tau) \overline{k}_{j'}^B\left(\tau'\right) \overline{\Pi}_{jj'}^{AB}\left(\tau, \tau'\right) \right. \right.$$

$$\left. \left. + 2 \int_{t_0}^{t_1} dt \int_0^{\beta\hbar} d\tau \sum_j \sum_i \overline{k}_j^A(\tau) k_i^B(t) \widetilde{\Pi}_{ji}^{AB}\left(\tau, t\right) \right] \right\} \tag{56}$$

where the indices i, i' were used for real time functions, while j, j' for imaginary time functions. The introduced double-time functions are actually correlation functions of the noises:

$$\Pi_{ii'}^{AB}\left(t, t'\right) = \left\langle z_i^A(t) z_{i'}^B\left(t'\right) \right\rangle_{\{z, \overline{z}\}} \equiv \Pi_{i'i}^{BA}\left(t', t\right) \tag{57}$$

$$\widetilde{\Pi}_{ji}^{AB}\left(\tau, t\right) = \left\langle \overline{z}_j^A(\tau) z_i^B\left(t\right) \right\rangle_{\{z, \overline{z}\}} \tag{58}$$

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$$\overline{\Pi}_{jj'}^{AB}\left(\tau,\tau'\right) = \left\langle \overline{z}_j^A(\tau)\overline{z}_{j'}^B\left(\tau'\right)\right\rangle_{\{z,\overline{z}\}} \equiv \overline{\Pi}_{j'j}^{BA}\left(\tau',\tau\right) \tag{59}$$

Note that $\Pi_{ii'}^{AB}\left(t,t'\right)$ and $\overline{\Pi}_{jj'}^{AB}\left(\tau,\tau'\right)$ form symmetric matrices. In the above equations each angle brackets $\left\langle \ldots \right\rangle_{\{z,\overline{z}\}}$ term corresponds to the stochastic averaging over the noises $\{z,\overline{z}\} = \left\{z_i^A(t),\overline{z}_j^A(\tau)\right\}$ with a Gaussian distribution function. These are actually path integrals in their own right as the noises depend on time, see details in Ref. [127].

Similarly to the method developed in Ref. [127], for each A we introduce four functions for the real time $(i = 1,\ldots,4)$ and two functions for the imaginary one $(j = 1,2)$:

$$k^A(t) = \begin{pmatrix} k_1^A(t) \\ k_2^A(t) \\ k_3^A(t) \\ k_4^A(t) \end{pmatrix} = \begin{pmatrix} v_A(t)/\hbar \\ 0 \\ r_A(t)/\hbar \\ 0 \end{pmatrix}, \quad \overline{k}^A(\tau) = \begin{pmatrix} \overline{k}_1^A\left(\tau\right) \\ \overline{k}_2^A\left(\tau\right) \end{pmatrix} = \begin{pmatrix} i\overline{u}_A\left(\tau\right)/\hbar \\ 0 \end{pmatrix} \tag{60}$$

which correspond to the noises as follows:

$$z^A(t) = \begin{pmatrix} z_1^A(t) \\ z_2^A(t) \\ z_3^A(t) \\ z_4^A(t) \end{pmatrix} \equiv \begin{pmatrix} \eta_A(t) \\ \eta_A^*(t) \\ \nu_A(t) \\ \nu_A^*(t) \end{pmatrix}, \quad \overline{z}^A(\tau) = \begin{pmatrix} \overline{z}_1^A\left(\tau\right) \\ \overline{z}_2^A\left(\tau\right) \end{pmatrix} \equiv \begin{pmatrix} \overline{\mu}_A\left(\tau\right) \\ \overline{\mu}_A^*\left(\tau\right) \end{pmatrix} \tag{61}$$

The rational for choosing three pairs of complex conjugate noises $(\eta_A(t),\eta_A^*(t))$, $(\nu_A(t),\nu_A^*(t))$ and $(\overline{\mu}_A(\tau),\overline{\mu}_A^*(\tau))$ for each nuclear degree of freedom A is as follows: (i) the noises must be complex as their corresponding correlation functions are in general complex (see below); (ii) we chose pairs of complex conjugate noises to ensure that the Gaussian distribution associated with them is real; our six complex noises are equivalent to choosing six *real* noises; (iii) three pairs of noises is a minimal possible set of noises necessary to establish the mapping we need as for each A there are *three* "variables" in the double integral (49): $v_A(t)$, $r_A(t)$ and $\overline{u}_A(\tau)$.

Then, the right hand side of Eq. (56) can be exactly mapped to the second order effective action in Eq. (49) if the following mapping conditions are satisfied for the correlation functions of the noises:

$$\Pi_{11}^{AB}\left(t,t'\right) \equiv \left\langle \eta_A(t)\eta_B\left(t'\right)\right\rangle_{\{z,\overline{z}\}} = \hbar^2 L_{AB}\left(t,t'\right) \tag{62}$$

$$\Pi_{31}^{AB}\left(t,t'\right) \equiv \left\langle \nu_A(t)\eta_B\left(t'\right)\right\rangle_{\{z,\overline{z}\}} = \frac{\hbar^2}{2} K_{AB}\left(t,t'\right) \tag{63}$$

$$\widetilde{\Pi}_{11}^{AB}\left(\tau,t\right) \equiv \left\langle \overline{\mu}_A(\tau)\eta_B\left(t\right)\right\rangle_{\{z,\overline{z}\}} = -\hbar^2 Y_{AB}^{\rceil\lceil}\left(\tau,t\right) \tag{64}$$

$$\overline{\Pi}_{11}^{AB}\left(\tau,\tau'\right) \equiv \left\langle \overline{\mu}_A(\tau)\overline{\mu}_B\left(\tau'\right)\right\rangle_{\{z,\overline{z}\}} = \hbar^2 \overline{L}_{AB}\left(\tau,\tau'\right) \tag{65}$$

$$\Pi_{33}^{AB}\left(t,t'\right) \equiv \left\langle \nu_A(t)\nu_B\left(t'\right)\right\rangle_{\{z,\overline{z}\}} = 0, \quad \widetilde{\Pi}_{13}^{AB}\left(\tau,t\right) \equiv \left\langle \overline{\mu}_A(\tau)\nu_B\left(t\right)\right\rangle_{\{z,\overline{z}\}} = 0 \tag{66}$$

Other correlation functions are not required. Note that the correlation functions $\Pi_{11}^{AB}\left(t,t'\right)$ and $\overline{\Pi}_{11}^{AB}\left(\tau,\tau'\right)$ are automatically symmetric, as required, due to the symmetry of the objects $L_{AB}\left(t,t'\right)$ and $\overline{L}_{AB}\left(\tau,\tau'\right)$, respectively (see Eqs. (50) and (52)).

We see that the noises satisfy certain correlations, which are related to the electronic Green's functions. The correlation functions above do not necessarily depend on the time difference; most likely they depend on both times. It is seen that the correlation functions are complex, see Eqs. (50)-(55), which justifies the choice we have made for the noises (61) to be complex.

2.6 Nuclei only (reduced) density matrix

Because of the established mapping, the contribution of the second order effective action can be replaced with an average $\left\langle \cdots \right\rangle_{\{z,\overline{z}\}}$ of a product of three fully independent exponential terms:

$$\exp\left\{\frac{i}{\hbar}\int_{t_0}^{t_1} dt \sum_A \left(\eta_A(t) + \frac{\nu_A(t)}{2}\right)u_A(t)\right\} \exp\left\{-\frac{i}{\hbar}\int_{t_0}^{t_1} dt \sum_A \left(\eta_A(t) - \frac{\nu_A(t)}{2}\right)u_A'(t)\right\}$$

$$\times \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \sum_A \overline{\mu}_A\left(\tau\right)\overline{u}_A(\tau)\right\}$$

Therefore, Eq. (30) can now be rewritten as the average over the Gaussian noises,

$$\widehat{\rho}_{ions}(t_1) = \left\langle \widehat{\rho}_{ions}^{S}(t_1) \right\rangle_{\{z,\overline{z}\}} \tag{67}$$

where the superscript S indicates that the density matrix operator $\widehat{\rho}_{ions}^{S}$ corresponds to a particular manifestation of the nosises, and

$$\left\langle x_1 \left| \widehat{\rho}_{ions}^{S}(t_1) \right| x_0 \right\rangle = \int dx_2 dx_3 \left\langle x_1 \left| \int \mathcal{D}x(t) e^{iS_1^+/\hbar} \right| x_2 \right\rangle$$

$$\times \left\langle x_2 \left| \frac{Z_2^0}{Z_0} \int \mathcal{D}\overline{x}(\tau) e^{-\overline{S}_1/\hbar} \right| x_3 \right\rangle \left\langle x_3 \left| \int \mathcal{D}x'(t) e^{-iS_1^-/\hbar} \right| x_0 \right\rangle \tag{68}$$

is its corresponding matrix element. It contains the following real and imaginary times actions acting on each track of γ,

$$S_1^+ = \int_{t_0}^{t_1} dt \left\{ L_1(t) + \sum_A \left[i\hbar Y_A^<(t) + \left(\eta_A(t) + \frac{\nu_A(t)}{2} \right) \right] u_A(t) \right\} \tag{69}$$

$$S_1^- = \int_{t_0}^{t_1} dt \left\{ L_1(t) + \sum_A \left[i\hbar Y_A^<(t) + \left(\eta_A(t) - \frac{\nu_A(t)}{2} \right) \right] u'_A(t) \right\} \tag{70}$$

$$\overline{S}_1 = \int_0^{\beta\hbar} d\tau \left\{ \overline{L}_1(\tau) + \sum_A \left[-i\hbar \overline{Y}_A^<(\tau) + \overline{\mu}_A(\tau) \right] \overline{u}_A(\tau) \right\} \tag{71}$$

where $L_1(t)$ is the Lagrangian of an isolated nuclear subsystem, $\overline{L}_1(\tau)$ being its corresponding Euclidean counterpart; the electron-nuclear coupling enters here via the first order and noise terms (expressions with the square brackets). The actions above imply the following *effective Hamiltonians* acting on each track of the contour γ:

$$\widehat{H}_\pm(t) = \mathcal{H}_1(t) - \sum_A \left[i\hbar Y_A^<(t) + \left(\eta_A(t) \pm \frac{\nu_A(t)}{2} \right) \right] u_A \tag{72}$$

$$\overline{H}(\tau) = \mathcal{H}_1^0 + \sum_A \left[-i\hbar \overline{Y}_A^<(\tau) + \overline{\mu}_A(\tau) \right] u_A \tag{73}$$

where $u_A = x_A - \langle x_A \rangle_t$ for the real time Hamiltonians $\widehat{H}_\pm(t)$, while $u_A = x_A - x_A^0$ for the imaginary time one, $\overline{H}(\tau)$.

In Eq. (68) the density matrix is factorised and that enables one to write an *exact* expression for the reduced (nuclei only) density matrix operator (see Appendix A and Ref. [127]), for the given manifestation of the noises, as follows:

$$\widehat{\rho}_{ions}^{S}(t) = \widehat{U}_+(t, t_0) \widehat{\rho}_0^{S} \widehat{U}_-(t_0, t) \tag{74}$$

where $\widehat{\rho}_0^{S} \equiv \widehat{\rho}_{ions}^{S}(t_0)$ is the initial reduced density matrix (for the same noises), to be discussed below, and two propagation operators have been introduced on each part of the horizontal track

$$\widehat{U}_+(t, t_0) = \widehat{\mathcal{T}}_+ \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t dt' \, \widehat{H}_+(t') \right\} \tag{75}$$

$$\widehat{U}_-(t_0, t) = \widehat{\mathcal{T}}_- \exp \left\{ \frac{i}{\hbar} \int_{t_0}^t dt' \, \widehat{H}_-(t') \right\} \tag{76}$$

which satisfy the following equations of motion:

$$i\hbar \partial_t \widehat{U}_+(t, t_0) = \widehat{H}_+(t) \widehat{U}_+(t, t_0) \tag{77}$$

$$i\hbar \partial_t \widehat{U}_-(t_0, t) = -\widehat{U}_-(t_0, t) \widehat{H}_-(t) \tag{78}$$

In the above equations $\widehat{\mathcal{T}}_+$ and $\widehat{\mathcal{T}}_-$ are the corresponding time-ordering operators on the upper (forward) and lower (backward) tracks of the contour γ. Note that the density matrix operator (74) is not normalised to unity at any time t, $\mathrm{Tr}_N\left(\widehat{\rho}_{ions}^{S}(t)\right) \neq 1$, although the final density matrix (67) is, $\mathrm{Tr}_N\left(\widehat{\rho}_{ions}(t)\right) = 1$ (the trace is understood here as being taken over the Hilbert subspace of the nuclei subsystem).

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2.7 Initial preparation of the system

In order to obtain the density matrix at real times, $\widehat{\rho}_{ions}^S(t)$ (for the given manifestation of the noises), one has to first determine the corresponding initial density matrix $\widehat{\rho}_0^S$. It can be found as the result of the propagation of an auxiliary density matrix $\widehat{\rho}^S(\tau)$ in imaginary time,

$$\widehat{\rho}_0^S \equiv \widehat{\rho}^S(\tau)\big|_{\tau=\beta\hbar}, \quad \widehat{\rho}^S(\tau) = \frac{Z_2^0}{Z_0}\widehat{U}^S(\tau) = \xi\widehat{U}^S(\tau) \tag{79}$$

where the imaginary time propagator

$$\widehat{U}^S(\tau) = \overline{\mathcal{T}}\exp\left\{-\frac{1}{\hbar}\int_0^\tau d\tau'\,\overline{H}(\tau')\right\} \tag{80}$$

has been defined, $\widehat{U}^S(0) = \widehat{1}$, that satisfies the following equation of motion in imaginary time:

$$-\hbar\partial_\tau\widehat{U}^S(\tau) = \overline{H}(\tau)\widehat{U}^S(\tau) \tag{81}$$

with $\overline{\mathcal{T}}$ being the corresponding time-ordering operators on the vertical (down) track of the contour γ. Of course, the operator $\widehat{\rho}^S(\tau)$ is not normalised to unity for any τ.

At $t = t_0$ we have the boundary condition,

$$\widehat{\rho}_{ions}^S(t_0) = \widehat{\rho}_0^S \equiv \widehat{\rho}^S(\tau)\big|_{\tau=\beta\hbar} \tag{82}$$

Note that here $\widehat{\rho}_{ions}^S(t_0)$ (or $\widehat{\rho}_0^S$) is defined up to (yet unknown) scaling factor ξ, Eq. (79). This factor can be obtained by noticing that the *exact initial density matrix* of the nuclear subsystem is obtained after averaging over the noises $\{\overline{\mu}_A(\tau)\}$,

$$\widehat{\rho}_0 \equiv \widehat{\rho}_{ions}(t_0) = \left\langle\widehat{\rho}_0^S\right\rangle_{\{\overline{\mu}_A\}} \tag{83}$$

Note that correlations with the real time noises are irrelevant in the case of the initial equilibration. Then, a subsequent normalisation of the exact inital density matrix operator $\widehat{\rho}_0$ should fix the scaling factor ξ.

Since the constant pre-factor $\xi = Z_2^0/Z_0$ does not depend on the noises (it only depends on the initial Hamiltonian) and hence is the same for each evolution of $\widehat{\rho}_{ions}^S(t)$, i.e. for any particular manifestation of the noises, it can be determined in practice by running a certain number of *representative* imaginary time evolutions as described below.

From this point on we shall be using a matrix representation of the density matrix operators and related quantities by employing an appropriate basis set $\{\chi_i(x)\}$ that depends on all nuclear coordinates x. To obtain the numerical prefactor ξ and the initial density matrix, it is convenient to propagate numerically the matrix $\mathbf{U}^S(\tau) = \left(U_{ij}^S(\tau)\right)$ associated with the auxiliary operator $\widehat{U}^S(\tau)$ (we shall remove the hat from operators when indicating their matrix representation):

$$-\hbar\partial_\tau U_{ij}^S(\tau) = \sum_k \overline{H}_{ik}(\tau)U_{kj}^S(\tau) \tag{84}$$

where

$$\overline{H}_{ik}(\tau) = \langle\chi_i|\mathcal{H}_1^0|\chi_k\rangle + \sum_A\left[-i\hbar\overline{Y}_A^<(\tau) + \overline{\mu}_A(\tau)\right]\langle\chi_i|u_A|\chi_k\rangle \tag{85}$$

is the matrix element of the Hamiltonian (73). One must use the unit matrix as the initial condition in solving these equations, $\mathbf{U}^S(\tau = 0) = \mathbf{1} = (\delta_{ij})$. Then the normalisation factor is obtained via $\xi = 1/\left\langle\xi_0^S\right\rangle_{\{\overline{\mu}_A\}}$, where $\xi_0^S = \text{tr}\left(\mathbf{U}^S(\beta\hbar)\right)$ is the trace of the auxiliary matrix corresponding to the given run. Note that this calculation, if required, enables one also to determine the matrix corresponding to the exact initial density matrix $\rho^0 = \left(\rho_{ij}^0\right)$, where $\rho_{ij}^0 = \langle\chi_i|\widehat{\rho}_0|\chi_j\rangle$, as $\rho_{ij}^0 = \xi\left\langle U_{ij}^S\right\rangle_{\{\overline{\mu}_A\}}$; it is now properly normalised, $\text{tr}\left(\rho^0\right) = 1$.

Having obtained the normalisation factor, the real time simulations of the matrix $\rho_{ions}(t) = \left(\langle\chi_i|\widehat{\rho}_{ions}(t)|\chi_j\rangle\right)$ can be initiated. We first run the imaginary time evolution to $\tau = \beta\hbar$ starting from the auxiliary density matrix with elements $\rho^S(0) = \left(\rho_{ij}^S(0)\right) = (\xi\delta_{ij})$. Using the obtained matrix $\left(\rho_{ij}^S(\beta\hbar)\right)$ as the initial condition for $\rho_{ions}^S(t_0)$, one proceeds with the real time run. This procedure ensures that, at any time $t \geq t_0$, the density matrix $\left\langle\rho_{ions}^S(t)\right\rangle_{\{z,\overline{z}\}}$, sampled over all noises, will be properly normalised. Sampling over all the real time runs, the total reduced density matrix, $\rho_{ions}(t)$, at any time $t \geq t_0$ is obtained.

Alternatively, one may run many imaginary + real time simulations from $\rho^S(0) = \left(\rho^S_{ij}(0)\right) = \left(\delta_{ij}\right)$, and then determine the normalisation factor ξ by sampling the density matrix at some particular time $t \geq t_0$ and then normalising. Then the actual reduced density matrix $\rho_{ions}(t)$ is obtained by scaling the calculated density at all times by ξ.

In any case, the expectation value $\left\langle \widehat{O} \right\rangle_t$ of any nuclear-only operator $\widehat{O}$ is calculated by taking the trace of the product of the matices $\rho_{ions}(t)$ (after normalisation) and $\mathbf{O} = (O_{ij})$,

$$\left\langle \widehat{O} \right\rangle_t = \sum_{ij} (\rho_{ions}(t))_{ij} O_{ji} = \mathrm{tr}\left(\rho_{ions}(t)\mathbf{O}\right)$$

Equations (74) and (79) present the central result of this paper. They perform *an exact transition* from the path integrals of the reduced density matrix of nuclei to its operator form. The path integrals were used as an intermediate device to introduce the stochastic fields, and, by means of the real-imaginary time Hubbard-Stratonovich transformation, to factorize the influence functional and hence to make the reverse transformation to the operator representation possible.

2.8 Equations of motion for nuclei

Direct propagation of the observables in real time is also possible. This may be numerically more preferable since the density matrix scales quadratically with the number n of the nuclear degrees of freedom, while the number of observables will scale linearly with n. We assume in what follows that the normalisation prefactor ξ is known, and hence the initial density matrix $\rho^S_{ions}(t_0)$, obtained by propagating in imaginary time the auxiliary matrix $\rho^S(\tau)$, is also known.

Having obtained an explicit expression for the operator of the density matrix of the nuclei, Eq. (74), we can differentiate it with respect to time. Using the equations of motion for the propagation operators, Eqs. (77) and (78), one can easily obtain an equation of motion for the reduced density matrix:

$$i\hbar \partial_t \widehat{\rho}^S_{ions}(t) = \widehat{H}_+(t)\widehat{\rho}^S_{ions}(t) - \widehat{\rho}^S_{ions}(t)\widehat{H}_-(t)$$

$$= \left[\mathcal{H}_1(t), \widehat{\rho}^S_{ions}(t)\right]_- - \sum_A \left\{ \left(i\hbar Y_A^<(t) + \eta_A(t)\right)\left[x_A, \widehat{\rho}^S_{ions}(t)\right]_- + \frac{\nu_A(t)}{2}\left[u_A(t), \widehat{\rho}^S_{ions}(t)\right]_+ \right\} \tag{86}$$

where $u_A(t) = x_A - \langle x_A \rangle_t^S$ is the displacement operator. The equation of motion contains both commutators and anticommutators, indicated with the minus and plus subscripts, respectively. As expected [128, 127], the dynamical evolution of the density matrix of an open system (the nuclei) contains the anitcommutator and hence is not Hamiltonian.

Correspondingly, an equation of motion for the expectation value of an arbitrary *nuclear-only* operator $\widehat{O}$ (for a particular realization of the noises, indicated again by the superscript S) reads:

$$i\hbar \partial_t \left\langle \widehat{O} \right\rangle_t^S = \left\langle \left[\widehat{O}, \mathcal{H}_1(t)\right]_- \right\rangle_t^S - \sum_A \left\{ \left(i\hbar Y_A^<(t) + \eta_A(t)\right)\left\langle \left[\widehat{O}, x_A\right]_- \right\rangle_t^S + \frac{\nu_A(t)}{2}\left\langle \left[\widehat{O}, u_A(t)\right]_+ \right\rangle_t^S \right\} \tag{87}$$

where $\left\langle \widehat{O} \right\rangle_t^S = \mathrm{Tr}_N\left(\widehat{\rho}^S_{ions}(t)\widehat{O}\right)$. As one can see, this equation contains only real time noises; however, it is to be emphasized that the real time noises are correlated with the imaginary time noises used to generate the initial auxiliary density matrix. In general, if transient effects (immediately after initial equilibration) are of interest, these correlations must be taken into account in calculating the real time evolution.

Applying Eq. (87) to the unity operator, $\widehat{O} = \widehat{1}$, one obtains an equation for the time evolution of the trace $\xi^S(t) = \mathrm{Tr}_N\left(\widehat{\rho}^S_{ions}(t)\right)$ of the density matrix for the given stochastic run:

$$\partial_t \xi^S(t) = -\frac{1}{i\hbar}\sum_A \nu_A(t)\langle u_A(t)\rangle_t^S$$

Since by definition $u_A(t) = x_A - \langle x_A \rangle_t^S$, then $\langle u_A(t)\rangle_t^S = 0$. This means that the trace of the density matrix remains constant during each stochastic run in real time, being equal to its initial value, $\xi^S(t) \equiv \xi_0^S$, at time t_0. Of course, these values will be different for different runs.

We shall now apply the above result to derive the time evolution of the nuclear positions, when $\widehat{O} \to x_A$. In this case we obtain:

$$\partial_t \langle x_A \rangle_t^S = \frac{1}{m_A} \langle p_A \rangle_t^S - \frac{1}{i\hbar} \sum_B \nu_B(t) \left[\langle x_A x_B \rangle_t^S - \langle x_A \rangle_t^S \langle x_B \rangle_t^S \right] \tag{88}$$

where $p_A = -i\hbar \frac{\partial}{\partial x_A}$ is the corresponding momentum operator. Note that an expression within the square brackets is in fact a fluctuation $\langle u_A(t) u_B(t) \rangle_t^S$.

Putting $\widehat{O} \to p_A$ in Eq. (87), we obtain a complimentary equation of motion for the momentum:

$$\partial_t \langle p_A \rangle_t^S = -\left\langle \frac{\partial U_1}{\partial x_A} \right\rangle_t^S + \left(i\hbar Y_A^<(t) + \eta_A(t) + \frac{\nu_A(t)}{2} \right) \xi_0^S - \frac{1}{i\hbar} \sum_B \nu_B(t) \left[\langle x_B p_A \rangle_t^S - \langle x_B \rangle_t^S \langle p_A \rangle_t^S \right] \tag{89}$$

where U_1 is the potential energy of nuclei due to the nuclei-nuclei interaction as well as due to a possible external field acting directly on nuclei. The last term in the square brackets contains another fluctuation, $\langle u_B(t) p_A \rangle_t^S$.

To proceed, we have to find an appropriate expression for the derivative of the potential U_1. In principle, one can try to write an equation of motion for the operator $\partial U_1 / \partial x_A$. It depends only on the atomic positions and hence only its commutator with momenta in the first term of Eq. (87) need to be considered, as well as the last - anticommutator - term in the same equation. The equation obtained in this way would also contain noises in its right hand side:

$$\partial_t \left\langle \frac{\partial U_1}{\partial x_A} \right\rangle_t^S = \sum_B \frac{1}{m_B} \left[-i\hbar \left\langle \frac{\partial^3 U_1}{\partial x_A \partial^2 x_B} \right\rangle_t^S + 2 \left\langle \frac{\partial^2 U_1}{\partial x_A \partial x_B} p_B \right\rangle_t^S \right] - \frac{1}{i\hbar} \sum_B \nu_B(t) \left[\left\langle \frac{\partial U_1}{\partial x_A} x_B \right\rangle_t^S - \left\langle \frac{\partial U_1}{\partial x_A} \right\rangle_t^S \langle x_B \rangle_t^S \right]$$

As a way of illustration, let us also work out this term within the harmonization approximation [125]. Indeed, expanding the potential energy U_1 in terms of nuclear displacements up to the second order,

$$U_1 \simeq U_1^0 + \sum_A \frac{\partial U_1 \left(\langle x \rangle_t^S \right)}{\partial \langle x_A \rangle_t^S} u_A(t) + \frac{1}{2} \sum_{AB} \frac{\partial^2 U_1 \left(\langle x \rangle_t^S \right)}{\partial \langle x_A \rangle_t^S \partial \langle x_B \rangle_t^S} u_A(t) u_B(t) \tag{90}$$

we obtain after differentiation and taking the average:

$$\left\langle \frac{\partial U_1}{\partial x_A} \right\rangle_t^S \simeq \frac{\partial U_1 \left(\langle x \rangle_t^S \right)}{\partial \langle x_A \rangle_t^S} \tag{91}$$

If we expand U_1 to the third order in the displacements, which is beyond the harmonization approximation, then the next term would contain fluctuations $\langle u_B(t) u_C(t) \rangle_t^S$. One can see that within the harmonization approximation the average (91) can easily be calculated directly from the mean atomic positions; no need in this case to construct a specific equation of motion for the average.

The obtained equations are not self-contained since they require knowledge of the time evolution of additional quantities such as $\langle x_A x_B \rangle_t^S$, $\langle x_A p_B \rangle_t^S$, $\left\langle \frac{\partial^2 U_1}{\partial x_A \partial x_B} \right\rangle_t^S$, and $\left\langle \frac{\partial U_1}{\partial x_A} x_B \right\rangle_t^S$. Writing the corresponding equations of motion for these quantities results in the appearance of higher order fluctuations. In the end, one obtains an infinite set of hierarchical equations of motion containing higher order fluctuations and higher order derivatives of the potential U_1. Correspondingly, in practice one has to terminate the hierarchy at some point to obtain a finite set of equations. This can be done by noticing that an average $\langle AB \rangle_t$ of a product of two operators A and B can always be written as a sum of their uncorrelated product and a fluctuation:

$$\langle AB \rangle_t = \langle A \rangle_t \langle B \rangle_t + [\langle AB \rangle_t - \langle A \rangle_t \langle B \rangle_t]$$

Hence, dropping the term with the fluctuation would express the average of the product as a product of the averages of simpler operators for which equations of motion may already exist. In addition, to deal with the operator corresponding to the derivatives of the potential energy U_1, the latter can be expanded in terms of atomic displacements up to an appropriate order as in Eq. (90), which would yield only averages of a product of positions and momenta operators to appear in the equations of motion.

Note that solution of the above equations requires knowledge of the initial (at $t = t_0$) mean values of all operators these equations contain. These are easily obtained, for each stochastic run, at the end of the imaginary time evolution via

$$\left\langle \widehat{O} \right\rangle_{t=t_0}^S = \text{tr} \left(\rho_{ions}^S(t_0) \mathbf{O} \right) \tag{92}$$

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3 Discussion and conclusions

In this paper we have considered a coupled system of nuclei and electrons. Either all or some of the nuclei are allowed to move. The goal was to obtain equations of motion for the nuclei taking full account of their interaction with the electrons and the electronic relaxation. Our method is based on a few ideas developed in Refs. [123, 45]. However, at variance with the mentioned work, in our method we do not invoke the partition approximation as the nuclei and electrons are considered fully coupled and thermalized at the initial time, which is more physically sound. In addition to that, we demonstrated, following the previous work [127], how one can get an exact expression for the reduced density matrix from its path integral representation.

The derived equations of motion for the atomic positions have a form of an infinite hierarchy of stochastic differential equations, containing three types of noises ($\{\eta_A(t)\}$, $\{\nu_A(t)\}$ and $\{\overline{\mu}_A(\tau)\}$) in real and imaginary times for each nuclear degree of freedom A that are considered explicitly (allowed to move). The noises are correlated with each other via various components of the electronic-only GF $\mathbb{G}$. We do not specify how this GF is to be calculated, this depends on the particular problem at hand. However, our analysis seems to suggest that no matter what kind of a system is actually considered, would it be a molecule under an electric pulse or a molecular junction under a bias, the general form of the equations of motion for the nuclei remains the same; it is *universal*. The particular problem under consideration imprints on the GF $\mathbb{G}$ and hence on the correlation functions of the noises to be considered to generate them.

The calculation proceeds in the following way:

1. During an imaginary time evolution, Eqs. (84) and (85), the system is initially prepared (thermalized) adopting a certain nuclear basis set $\{\chi_i(x)\}$. One starts from the unit auxiliary matrix at $\tau = 0$, i.e. $(U_{ij}(0)) = \mathbf{1}$, and then propagates it in time up to $\tau = \beta\hbar$. The trace of the obtained auxiliary matrix, ξ_0^S, is stored. This calculation requires generating only one set of noises, $\{\overline{\mu}_A(\tau)\}$, that are correlated via Eq. (65), and hence the knowledge of the electronic GF on the vertical track of the contour is only needed, $\mathbb{G}_{MM}^<(\tau, \tau')$ and $\mathbb{G}_{MM}^>(\tau, \tau')$, see Eqs. (46) and (54), as only they determine the function $\overline{L}_{AB}(\tau, \tau')$, Eq. (52), which enters the correlation of the noise. The calculations are repeated the necessary number of times for different noises, and the normalisation prefactor, $\xi = 1/\langle \xi_0^S \rangle_{\{\overline{\mu}_A\}}$, is worked out. The sampling is stopped when ξ is converged (does not change upon addition of new stochastic runs).

2. To propagate the nuclear system in real time, one has to decide upon termination at a certain order of the hierarchy of stochastic differential equations considered in section 2.8 by setting any higher order fluctuations and derivatives of the nuclear potential energy to zero. In the case of the potential energy this approximation simply corresponds to adopting a Taylor expansion of U_1 in terms of the nuclear displacements $u_A = x_A - \langle x_A \rangle_t^S$ terminated at a certain order; the harmonization approximation where all terms after the quadratic ones are set to zero being the simplest approximation. The equations adopted contain a finite number of specific expectation values $\left\langle \widehat{O}_1 \right\rangle_t^S$, $\left\langle \widehat{O}_2 \right\rangle_t^S$, etc. to propagate in time.

3. Then, using the adopted matrix representation, many time evolutions are run. Each such evolution consists of an imaginary run followed up by the real time one.

   (a) Diring the imaginary time run, one starts with the auxiliary matrix $\rho^S(\tau = 0) = (\xi\delta_{ij})$ and then propagates it up to $\tau = \beta\hbar$; then the value of the trace ξ_0^S is stored and the initial values of all expectation values $\left\langle \widehat{O}_1 \right\rangle_{t_0}^S$, $\left\langle \widehat{O}_2 \right\rangle_{t_0}^S$, etc. that are met in the equations of motion are also calculated using Eq. (92).

   (b) Then one has to propagate numerically those expectation values in real time employing a small time step Δt using the derived equations of motion for them from the terminated hierarchy. This calculation requires generating two sets of noises, $\{\eta_A(t)\}$ and $\{\nu_A(t)\}$, which are to be correlated not only between themselves, but also with the noises $\{\overline{\mu}_A(\tau)\}$ generated for the initial preparation of the system (point 3a above), for each particular run. The calculation of the correlation functions (62) - (64) requires obtaining all other components of the electronic GF $\mathbb{G}^<$, $\mathbb{G}^>$, $\mathbb{G}^\lceil$, and $\mathbb{G}^\rceil$ at progressive times, see Eqs. (50), (51), (53) and (55). The GFs depend on the actual positions of the atoms, $\langle x_A \rangle_t^S$, as these modify the electronic Hamiltonian. Therefore, the numerical solution of the equations of motion requires recalculating the GFs, and hence the correlation functions and the noises $\{\eta_A(t)\}$ and $\{\nu_A(t)\}$, at each consecutive time step (or after a certain number of such steps). The recalculation of the components of the GF ($\mathbb{G}^<$, $\mathbb{G}^>$, $\mathbb{G}^\rceil$ and $\mathbb{G}^\lceil$) can be done by solving their corresponding equations of motion (Kadanoff-Baym equations) numerically using e.g. the time-stepping technique; there is a significant experience in this regard (see e.g. the book [122], p. 472).

4. The calculation is repeated with different realizations of the noises, and the final result is obtained by sampling over all such calculations, i.e.

$$\langle x_A \rangle_t = \left\langle \langle x_A \rangle_t^S \right\rangle_{\{\eta_A, \nu_A, \overline{\mu}_A\}}, \quad \langle p_A \rangle_t = \left\langle \langle p_A \rangle_t^S \right\rangle_{\{\eta_A, \nu_A, \overline{\mu}_A\}}$$

and so on.

The described algorithm enables one not only to calculate the mean atomic trajectory $\langle x_A \rangle_t$ of atoms in the system, but also various their fluctuations from the mean trajectory. This naturally corresponds to the fact that nuclei in our method are considered fully quantum-mechanically.

Basically, only two approximations have been made in our theory: (i) the part of the Hamiltonian responsible for the interaction between electrons and nuclei (in the full-electron picture that would simply be the corresponding Coulomb interaction term) was considered up to the second order with respect to the displacements of the nuclei from either their instantaneous positions given by the mean atomic trajectory (real time evolution) or from their equilibrium positions (initial preparation corresponding to the imaginary time evolution, Eqs. (79) and (81)); (ii) the electronic GF was expanded only up to the first order with respect to such displacements, Eq. (37). Both approximations are consistent with each other and correspond to the harmonization picture. No other approximations have been made.

Note that the harmonization approximation applied here does not assume small electron-nuclear interaction; instead, it adopts a view that only small fluctuations of atomic positions from their either equilibrium positions (initial preparation of the system) or the mean trajectory (during the real time evolution) are essential. This implies an application of this method to not too large temperatures. At the same time, by considering time-variable mean positions around which the electron-nuclear interaction is expanded, rather than fixed such positions (as e.g. equilibrium positions), our methods effectively goes beyond the harmonic approximation and does not assume that such interaction is weak.

In spirit, our method is similar to the CEID method [109] - [113], which also results in an infinite hierarchy of differential equations for various expectation values of nuclear related operators. The main difference (apart from the derivation itself that is rather different) is in the way electrons and their interaction with nuclei are accounted for. If in CEID the electrons are accounted for approximately, the formulation via NEGF developed here has a potential of being more general and rigorous.

One may wonder how our method is related to Generalised Langevin Equation (GLE) methods, see e,g. [125] and references therein, which can also be used to consider atomic trajectories of nuclei treated as an open system (in that case the bath was considered a set of harmonic oscillators, however). In GLE method equations of motion for mean atomic trajectories have the form of stochastic differential equations with a time integral term (friction), which corresponds to a memory accumulated during preceding times. Formally, our equations of motion have a very different form; for instance, there is no memory time integrals at all in our equations. This observation, however, may be too rushed: indeed, we have to deal with more than one equation: there are in fact two sets. One consists of the equations for atomic positions and momenta, and the other - of other equations for various fluctuations and derivatives of the potential U_1. Therefore, solving formally for all fluctuations from the second set (this solution would have time integral terms) and substituting the obtained expressions into the equations for the positions and momenta of the first set, Eqs. (88) and (89), an integral memory-like term would appear. However, at this stage these are just rather general observations; detailed execution of the above program is left for future work.

The theoretical framework proposed in this paper is rather general. Its application to a particular system is imprinted in the nuclear-only potential energy U_1 and in the electronic GF. The form of the equations of motion for atoms is, however, *universal*. This method we hope will also contribute to the discussion [65, 31, 39, 45, 63] of current induced forces although, when the atomic nuclei are considered as quantum, the notion of a classical "atomic force" is not strictly meaningful (quantum nuclei were initially considered also in [45] although in the end the authors went back to classical nuclei when writing a GLE for them).

The other point is that our method is fully numerical: to obtain the atomic trajectory (and their fluctuations) one has to solve the equations of motion discussed above on a computer. Therefore, this method may not only be used for perform actual calculations on realistic systems; it can serve as a benchmark for various approximate methods.

There are several important technical issues that require further thorough investigation. The main fundamental point is related to the level at which the hierarchy of equations of motion can be safely terminated; surely this should depend on the problem at hand. The other point is related to the time step to choose in order to integrate the equations of motion numerically; we expect that this time step may be longer than the electronic (femtosecond) range, but might be shorter than the timescale of atomic vibrations. Finally, and most importantly, an efficient

implementation of the method must be developed. The mentioned points require detailed investigations and are left for future work.

Finally, we note that our method can only be used specifically for obtaining atomic trajectories (or expectation values of any nuclear-related operators). It cannot be used for calculating expectation values associated with electronic operators such as the electronic density or current *if* one is willing to remain outside the adiabatic picture. In this most general case in order to obtain expectation values of electronic operators along the mean atomic trajectory as functions of time, other methods need to be developed. These are presently being developed in our laboratory. Note, however, that if the nuclear movement can be considered as being relatively slow, the electronic-only GF $\mathbb{G}$ obtained along the mean trajectory within our method can be used for such a calculation. This would however correspond to the adiabatic calculation in which no electron-nuclear interaction is considered explicitly, but the atomic trajectories change in time.

We hope that this work will stimulate further research on atomic dynamics of general non-equilibrium systems, e.g. in developing new wavepacket methods based on the equation of motion (86) for the reduced (ionic) density matrix.

Appendix A

Consider a general propagation operator

$$\widehat{U}_\gamma\left(z, z'\right) = \widehat{\mathcal{T}}_\gamma \exp\left\{-\frac{i}{\hbar} \int_{z'}^{z} \mathcal{H}\left(z_1\right) dz_1\right\}$$

between any two points $z, z' \in \gamma$ on the contour shown in Fig. 1. In practice, to derive Eq. (16), we shall only need to consider three particular cases, where both times lie *on the same* track: (i) both $z = t$ and $z' = t'$ are on the upper track, $t > t'$; (ii) $z = t$ and $z' = t'$ are on the lower tack with $z > z'$ (meaning that $t < t'$), and (iii) $z = t_0^- - i\tau$ and $z' = t_0^-$ are on the vertical track with $z > z'$ ($\tau > 0$). However, we proceed with the derivation in the general case and will consider these particular cases at the end of the calculation.

The propagator satisfies the semi-group property, $\widehat{U}_\gamma\left(z, z'\right) = \widehat{U}_\gamma\left(z, z_1\right) \widehat{U}_\gamma\left(z_1, z'\right)$ and also $\widehat{U}_\gamma\left(z, z\right) = 1$.

We are interested in writing the propagator in the coordinate representation with respect to the nuclear positions x_0 and x (from region 1). Let us split the part of the contour between z' and z by n "equidistant" points with the distance between them $|\epsilon| \sim 1/n$. Note that the meaning of $\epsilon \equiv \Delta z$ depends on where Δz is: it is equal to Δt or $-\Delta t$ on the horizontal upper or lower tracks, respectively, and to $-i\Delta\tau$ on the vertical track. Then, writing the propagator as a product of propagators over each interval, we obtain - by inserting the resolution of identity $\int |x\rangle \langle x| \, dx = 1$ in appropriate places - an expression:

$$\left\langle x_f \left| \widehat{U}_\gamma\left(z, z'\right) \right| x_0 \right\rangle = \int dx_{n-1} \cdots dx_1 \left\langle x_f \left| \widehat{U}_\gamma\left(z, z_{n-1}\right) \right| x_{n-1} \right\rangle \cdots \left\langle x_1 \left| \widehat{U}_\gamma\left(z_1, z_0\right) \right| x_0 \right\rangle$$

Here x_j is a vector of a particular instance of all nuclei degrees of freedom associated with the time z_j on the contour, with $j = 0, \ldots, n$. We set $z_n = z$ and $z_0 = z'$; also, x_0 corresponds to z' and x_f to z.

The Hamiltonian in the propagator $\mathcal{H} = (K_1 + K_2) + (V_1(x) + V_{12}(x) + V_2)$ consists of kinetic and potential energy terms for each region, as well as of the interaction V_{12} between them. For small ϵ every elementary propagator can be factorised,

$$\widehat{U}_\gamma\left(z_{j+1}, z_j\right) \simeq e^{-i\epsilon(K_1+K_2)/\hbar} e^{-i\epsilon(V_1+V_2+V_{12})/\hbar}$$

leading to

$$\left\langle x_{j+1} \left| \widehat{U}_\gamma\left(z_{j+1}, z_j\right) \right| x_j \right\rangle \simeq e^{-i\epsilon K_2/\hbar} e^{-i\epsilon(V_1(x_j)+V_2+V_{12}(x_j))/\hbar} \left\langle x_{j+1} \left| e^{-i\epsilon K_1/\hbar} \right| x_j \right\rangle$$

The remaining matrix element is worked out in a usual way by inserting twice the resolution of identity $\int |p\rangle \langle p| \, dp = 1$ with respect to the vector p of all nuclear momenta, and using the fact that

$$\langle x | p \rangle = \left(\prod_A \frac{1}{\sqrt{2\pi\hbar}}\right) e^{ipx/\hbar}$$

and

$$\langle p | e^{-i\epsilon K_1/\hbar} | p' \rangle = \delta\left(p - p'\right) e^{-iK_1(p)\epsilon/\hbar}$$

We obtain:

$$\langle x_{j+1}| \widehat{U}_\gamma (z_{j+1}, z_j) |x_j \rangle = \left[\prod_A \left(\frac{m_A}{2\pi\hbar i\epsilon} \right)^{1/2} \right] \exp\left\{ \frac{i\epsilon}{\hbar} \left[\sum_A \frac{m_A}{2} \left(\frac{x_{A,j+1} - x_{A,j}}{\epsilon} \right)^2 - V_1 (x_j) \right] \right\}$$

$$\times \exp\left\{ -\frac{i\epsilon}{\hbar} K_2 \right\} \exp\left\{ -\frac{i\epsilon}{\hbar} [V_{12} (x_j) + V_2] \right\}$$

where use has been made of the fact that the positions and momenta of region 1 commute with those of region 2.

Correspondingly, the coordinate representation of the propagator is a multiple integral of a product of the above type of terms calculated for different positions x_j:

$$\left\langle x_f \left| \widehat{U}_\gamma (z, z') \right| x_0 \right\rangle \simeq \int dx_{n-1} \cdots dx_1 \left[\prod_A \left(\frac{m_A}{2\pi\hbar i\epsilon} \right)^{n/2} \right] \exp\left\{ \frac{i\epsilon}{\hbar} \sum_{j=0}^{n-1} \left[\sum_A \frac{m_A}{2} \left(\frac{x_{A,j+1} - x_{A,j}}{\epsilon} \right)^2 - V_1 (x_j) \right] \right\}$$

$$\times e^{-iK_2\epsilon/\hbar} e^{-i[V_{12}(x_{n-1})+V_2]\epsilon/\hbar} \cdots e^{-iK_2\epsilon/\hbar} e^{-i[V_{12}(x_j)+V_2]\epsilon/\hbar} \cdots e^{-iK_2\epsilon/\hbar} e^{-i[V_{12}(x_0)+V_2]\epsilon/\hbar} \tag{93}$$

The expression on the first line in the right hand side in the $n \to \infty$ limit (and hence when $|\epsilon| \to 0$) becomes the path integral associated with the action

$$S_1 [x(z)] = \int_{z'}^{z} L_1 (z_1) \, dz_1 = \int_{z'}^{z} (K_1 - V_1 (z_1)) \, dz_1$$

where the atomic velocities were defined with respect to the "time" $\epsilon \equiv \Delta z$ on the contour. Next, on the second line in Eq. (93) we have an *ordered* product of exponential operators, with times on γ increasing from right to left from z' to z. In the $n \to \infty$ limit these could then be written as a time ordered exponent

$$\widehat{U}_2 (z, z') = \widehat{\mathcal{T}}_\gamma \exp\left\{ -\frac{i}{\hbar} \int_{z'}^{z} \mathcal{H}_2 (z_1) \, dz_1 \right\}$$

where $\mathcal{H}_2 (z) = K_2 + V_2 + V_{12} (z)$ and the integral is taken between z' and z on the contour. Therefore, we have just proved an exact identity

$$\left\langle x_f \left| \widehat{U}_\gamma (z, z') \right| x_0 \right\rangle = \int_{x(z')=x_0}^{x(z)=x_f} \mathcal{D}x (z) \, e^{iS_1[x(z)]/\hbar} \widehat{U}_2 (z, z')$$

Clearly, this result is valid for the times z and z' lying anywhere on γ. Subtleties associated with factorization of the exponential operators in the $n \to \infty$ limit are rigorously discussed e.g. in Ref. [129].

Consider now the three cases we are actually interested in.

(i) Both times lie on the upper track: $z = t_1$ and $z' = t_0^+$. Then, $\epsilon = (t_1 - t_0)/n > 0$, and we recover Eqs. (7) and (8).

(ii) Both times lie on the lower track: $z = t_0^-$ and $z' = t_1$. Then, $\epsilon = (t_0 - t_1)/n < 0$, and we obtain the reverse time propagator:

$$\left\langle x_0 \left| \widehat{U} (t_0, t_1) \right| x_1 \right\rangle = \int_{x'(t_1)=x_1}^{x'(t_0)=x_0} \mathcal{D}x'(t) e^{-iS_1[x'(t)]/\hbar} \widehat{U}_2 (t_0, t_1)$$

where

$$\widehat{U}_2 (t_0, t_1) = \widehat{\mathcal{T}}_- \exp\left\{ \frac{i}{\hbar} \int_{t_0}^{t_1} [\mathcal{H}_2 (t') + \mathcal{H}_{12} (x' (t'))] \, dt' \right\} \equiv \widehat{U}_2^\dagger (t_1, t_0)$$

is the corresponding electronic propagator.

(iii) Both times lie on the vertical track: $z = t_0^- - i\tau$ and $z' = t_0^-$. In this case $\epsilon = -i\tau/n = -i\Delta\tau$, the atomic velocity $\Delta\overline{x}/\Delta z = i\Delta\overline{x}/\Delta\tau$ acquires an extra i, and hence the following identity results:

$$\left\langle x \left| \widehat{U}_\gamma (\tau, 0) \right| x_0 \right\rangle = \int_{\overline{x}(0)=x_0}^{\overline{x}(\tau)=x} \mathcal{D}\overline{x} (\tau) \, e^{-S_1^0[\overline{x}(\tau)]/\hbar} \widehat{U}_2 (\tau, 0)$$

where S_1^0 is the Euclidean action, and

$$\widehat{U}_2 (\tau, 0) = \overline{\mathcal{T}} \exp\left\{ -\frac{1}{\hbar} \int_0^\tau \left[\mathcal{H}_2^0 + \mathcal{H}_{12}^0 (\overline{x} (\tau')) \right] d\tau' \right\}$$

is the corresponding imaginary time propagator. In particular, when the initial Hamiltonian does not depend on the imaginary time and $\tau \equiv \beta\hbar$, the representation of the exponential operator $e^{-\beta\mathcal{H}^0}$ is recovered, Eqs. (13) and (14).

The obtained expressions enable one, when read from left to right, to replace the matrix elements of the propagation operators with appropriate partial path integrals over nuclear trajectories. This was used in section 2.2. However, if read from right to left, the same identities can be used to replace path integrals with the corresponding matrix elements of time-ordered propagators. In fact, this has been done in section 2.6 when going from Eq. (68) to (80), albeit for a much simpler case when only region 1 was present and hence there were no operators $\widehat{U}_2$ anymore.

Appendix B

Here we shall consider the case when region C that includes electron orbitals interacting with nuclear displacements does not contain all orbitals of the whole system. In particular, this case may correspond to a molecule on a surface, when the electron-nuclear interaction is included only for the molecule, or a case of a molecular junction, where this interaction is only considered explicitly for the central region between the leads.

To illustrate the general idea, we shall consider a molecular junction with the central region (region C) to which electrodes (leads) are attached. We shall adopt the simplest one-particle approximation for the leads, i.e. the following electronic Hamiltonian $\mathcal{H}_2$ for all times $t \geq t_0$ will be assumed:

$$\mathcal{H}_2(z) = \sum_{\alpha k} \epsilon_{\alpha k}(z) c_{\alpha k}^\dagger c_{\alpha k} + \sum_{nm} T_{nm}(z) c_n^\dagger c_m + \sum_n \sum_{\alpha k} \left[T_{\alpha k,n}(z) c_n^\dagger c_{\alpha k} + \text{h.c.} \right] + V_C \tag{94}$$

where the first term describes the leads, the second - the central system, and the third - interaction of the latter with the leads. The last term corresponds to electronic correlation effects which are only considered non-zero in the central region C, i.e. V_C only contains operators from this region. Multiple leads are assumed here designated by α. The index k numbers states of a particular lead.

The matrix elements in the Hamiltonian depend on z due to the following reasons. Firstly, the dependence on z of $\epsilon_{\alpha k}(z)$ comes from the fact that a time-dependent bias may be applied in the junction to the leads, i.e. each lead may be subjected to a particular potential $\phi_\alpha(t)$ for z lying on the horizontal tracks of γ; on the vertical track, corresponding to the initial preparation of the system, there is no bias applied. Secondly, the z dependence of the central region related matrix elements, $T_{nm}(z)$ and $T_{\alpha k,n}(z) = T_{n,\alpha k}^*(z)$, is entirely due to the fact that nuclei positions depend on z. Namely, on the horizontal tracks nuclei are clamped at $\langle x_A \rangle_t$ (and hence evolve in time), while their positions are set to the constant values x_A^0 on the vertical track.

The electronic Hamiltonian (94) can conveniently be rewritten in a simplified form:

$$\mathcal{H}_2(z) = \sum_{ab} h_{ab}(z) c_a^\dagger c_b + V_C \tag{95}$$

where the summation is run over all orbitals of the entire system, and

$$h_{\alpha k, \alpha' k'}(z) = \delta_{\alpha\alpha'} \begin{cases} \delta_{kk'} \left[\epsilon_{\alpha k} + \phi_\alpha(t) \right], & \text{if } z \in \text{horizontal track} \\ \delta_{kk'} \left(\epsilon_{\alpha k} - \mu \right) & \text{if } z \in \text{vertical track} \end{cases} \tag{96}$$

$$h_{\alpha k, n}(z) = \begin{cases} T_{\alpha k, n}(t), & \text{if } z \in \text{horizontal track} \\ T_{\alpha k, n}^0, & \text{if } z \in \text{vertical track} \end{cases} \tag{97}$$

$$h_{nm}(z) = \begin{cases} T_{nm}(t), & \text{if } z \in \text{horizontal track} \\ T_{nm}^0 - \mu\delta_{nm}, & \text{if } z \in \text{vertical track} \end{cases} \tag{98}$$

Here we included explicitly the electronic chemical potential for the Hamiltonian on the vertical track in accordance with the initial density matrix (12). As was mentioned, the time dependence of the matrix elements $T_{nm}(t)$ and $T_{\alpha k,n}(t) = T_{n,\alpha k}^*(t)$ on the horizontal tracks comes from the nuclear positions which are chosen as $\langle x_A \rangle_t$.

Correspondingly, the whole Hamiltonian governing the evolution of the electronic GF is, therefore,

$$H_2^\lambda(z) = \mathcal{H}_2(z) + \mathcal{H}_{12}^\lambda(z) = \sum_{ab} \left[h_{ab}(z) + \lambda V_{ab}(z) \right] c_a^\dagger c_b + V_C \tag{99}$$

Hence, the GF introduced above satisfies the usual equations of motion based on this Hamiltonian:

$$i\hbar\partial_z G_{ab}^\lambda(z, z') = \delta_{ab}\delta(z - z') + \sum_c \left[h_{ac}(z) + \lambda V_{ac}(z) \right] G_{cb}^\lambda(z, z') + \int_\gamma dz_1 \sum_{d \in C} \widetilde{\Sigma}_{ad}(z, z_1) G_{db}^\lambda(z_1, z') \tag{100}$$

$$-i\hbar\partial_{z'}G_{ab}^\lambda(z,z') = \delta_{ab}\delta(z-z') + \sum_c G_{ac}^\lambda(z,z')\left[h_{cb}(z') + \lambda V_{cb}(z')\right] + \int_\gamma dz_1 \sum_{d\in C} G_{ad}^\lambda(z,z_1)\widetilde{\Sigma}_{db}(z_1,z') \quad (101)$$

where

$$\delta(z-z') = \frac{d}{dz}\theta_{zz'} = \begin{cases} \delta(t-t'), & \text{if } z,z' \in \text{upper track} \\ -\delta(t-t'), & \text{if } z,z' \in \text{lower track} \\ i\delta(\tau-\tau') & \text{if } z,z' \in \text{vertical track} \\ 0, & \text{in all other cases} \end{cases} \quad (102)$$

which satisfies the usual filtering theorem on the contour γ for any "good" function $f(z)$:

$$\int_\gamma f(z')\,\delta(z-z')\,dz' = f(z)$$

and we have introduced an electronic self-energy matrix $\widetilde{\Sigma}_{CC}(z,z')$ defined only for orbitals in the central region. Note that the last term in Eq. (100) is only kept for $a \in C$, while in Eq. (101) it survives for $b \in C$.

Writing Eq. (100) in the matrix form for the blocks CC and αC, solving for $\mathbf{G}_{\alpha C}^\lambda$ and substituting it into the equation for $\mathbf{G}_{CC}^\lambda$, one obtains using the matrix notations:

$$i\hbar\partial_z \mathbf{G}_{CC}^\lambda(z,z') = \mathbf{1}_C\delta(z-z') + \left[\mathbf{h}_C(z) + \lambda\mathbf{V}_C(z)\right]\mathbf{G}_{CC}^\lambda(z,z') + \int_\gamma dz_1 \overline{\Sigma}_{CC}(z,z_1)\mathbf{G}_{CC}^\lambda(z_1,z') \quad (103)$$

where $\overline{\Sigma}_{CC}(z,z_1) = \Sigma_{CC}(z,z_1) + \widetilde{\Sigma}_{CC}(z,z_1)$ is the composed self-energy, containing, apart from the correlation component, also the self-energy of the electrodes [122]:

$$\Sigma_{CC}(z,z') = \sum_\alpha \Sigma_{CC}^\alpha(z,z') = \sum_\alpha \mathbf{h}_{C\alpha}(z)\mathbf{g}_\alpha(z,z')\mathbf{h}_{\alpha C}(z') \quad (104)$$

Here $\mathbf{g}_\alpha(z,z')$ is the GF of the isolated lead α associated with the Hamiltonian $\mathbf{h}_\alpha(z)$. We have assumed that the leads do not directly interact. It is seen that the leads and correlation self-energies simply add up.

In the same way one can define the "unperturbed" GF, $\mathbb{G}(z,z')$, defined without the electron-nuclear coupling (section 2.3); it satisfies

$$i\hbar\partial_z\mathbb{G}_{CC}(z,z') = \mathbf{1}_C\delta(z-z') + \mathbf{h}_C(z)\mathbb{G}_{CC}(z,z') + \int_\gamma dz_1 \overline{\Sigma}_{CC}(z,z_1)\mathbb{G}_{CC}(z_1,z') \quad (105)$$

It is essential that $\mathbb{G}(z,z')$ is defined by the matrix $\mathbf{h}(z)$, which is the same on both horizontal tracks of γ. Note that, because of the time dependence of the nuclear positions on the horizontal tracks given by $\langle x_A\rangle_t$, the calculation of $\mathbb{G}(z,z')$ might be non-trivial. If such a dependence is ignored (and, e.g. replaced by the equilibrium positions x_A^0), then this GF can be calculated explicitly e.g. in the wide band approximation and in absence of electronic correlation [124, 130, 131].

The two functions $\mathbf{G}_{CC}^\lambda$ and $\mathbb{G}_{CC}$ are related by a Dyson-type equation. To derive it, we rewrite Eqs. (103) and (105) in a symbolic form to keep simple notations:

$$(i\hbar\partial_z - \mathbf{h}_z)\mathbf{G}^\lambda = \mathbf{1}\delta + \lambda\mathbf{V}\mathbf{G}^\lambda + \overline{\Sigma}\mathbf{G}^\lambda \quad (106)$$

$$(i\hbar\partial_z - \mathbf{h}_z)\mathbb{G} = \mathbf{1}\delta + \overline{\Sigma}\mathbb{G} \quad (107)$$

Here convolutions are assumed in a product of any two-time quantities, e.g. in $\overline{\Sigma}\mathbf{G}^\lambda$. If we introduce the GF for the central region, $\mathbf{g}_C(z,z')$ (to be denoted simply by $\mathbf{g}$ in our symbolic notations), which satisfies $(i\hbar\partial_z - \mathbf{h}_z)\mathbf{g} = \mathbf{1}\delta$, then the two equations transform into:

$$\mathbf{G}^\lambda = \mathbf{g} + \lambda\mathbf{g}\mathbf{V}\mathbf{G}^\lambda + \mathbf{g}\overline{\Sigma}\mathbf{G}^\lambda$$

$$\mathbb{G} = \mathbf{g} + \mathbf{g}\overline{\Sigma}\mathbb{G}$$

From the second equation $\mathbf{g} = \left(\mathbf{1} - \mathbf{g}\overline{\Sigma}\right)\mathbb{G}$, which, when used in the first, gives the required relationship,

$$\mathbf{G}^\lambda = \mathbb{G} + \lambda\mathbb{G}\mathbf{V}\mathbf{G}^\lambda$$

which has exactly the form of the Dyson equation (36).

Hence, in any case when the region C does not cover the whole system, the contribution of the rest of the system that does not interact directly with nuclear displacements in region 1 manifests itself in the properly defined self-energy which is simply added to the correlation self-energy of region C. Therefore, having this in mind, one can use only the block CC of the Green's Functions in the actual calculations.

Appendix C

Calculation of the contour integral in Eq. (37) requires a generalization of the Langreth rules [122] for the case when the Hamiltonian on different horizontal tracks is different, and there is an extra single variable function in the convolution, $\mathbf{V}(z)$. Only the lesser component is needed for our purposes here; however, we have to consider the cases of z being on the upper, lower and vertical tracks.

Therefore, let us consider an integral over the contour:

$$C(z, z') = \int_\gamma dz_1 \, A(z, z_1) \, V(z_1) \, B(z_1, z') \tag{108}$$

Performing the integration explicitly over each of the three tracks on γ, the following identities can be established:

$$C^<_{++}(t, t') = -i \int_0^{\beta\hbar} d\tau \, A_{+M} V_M B_{M+}$$

$$+ \int_{t_0}^{t_1} dt \left(A^r_{++} V_+ B^<_{++} + A^<_{++} V_+ B^a_{++} + A^<_{++} V_+ B^>_{++} - A_{+-} V_- B_{-+} \right) \tag{109}$$

$$C^<_{--}(t, t') = -i \int_0^{\beta\hbar} d\tau \, A_{-M} V_M B_{M-}$$

$$+ \int_{t_0}^{t_1} dt \left(A^r_{--} V_- B^<_{--} + A^<_{--} V_- B^a_{--} + A_{-+} V_+ B_{+-} - A^>_{--} V_- B^<_{--} \right) \tag{110}$$

$$C^<_{MM}(\tau, \tau') = \int_{t_0}^{t_1} dt \left(A_{M+} V_+ B_{+M} - A_{M-} V_- B_{-M} \right)$$

$$- i \int_0^{\beta\hbar} d\tau_1 \left(A^r_{MM} V_M B^<_{MM} + A^<_{MM} V_M B^a_{MM} + A^<_{MM} V_M B^>_{MM} \right) \tag{111}$$

Above, for simplicity of notations, the arguments of the functions are omitted; that should not cause any confusion as all integrals correspond to convolutions. Also, note that the retarded and advanced components can only be introduced when both times are positioned on the same track (either forward, backward or vertical).

Usual Langreth rules [122] are recognized here when there is no difference between the two horizontal tracks and the function $V(z) \equiv 1$. For instance, consider the first formula (109): in this case there is no difference between $A_{+-} = A^<$ and $A^<_{++}$, $V_+ = V_- \equiv 1$ and also, $B^>_{++} = B_{-+}$, so that the third and the fourth contributions in the real time integral cancel out, and we arrive at the usual rules for the lesser function. Also, both expressions (109) and (110) give identical results.

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