How Electronic Dynamics with Pauli Exclusion Produces Fermi-Dirac Statistics

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(Dated: 20 November 2014)

It is important that any dynamics method approaches the correct population distribution at long times. In this paper, we derive a one-body reduced density matrix dynamics for electrons in energetic contact with a bath. We obtain a remarkable equation of motion which shows that in order to reach equilibrium properly, rates of electron transitions depend on the density matrix. Even though the bath drives the electrons towards a Boltzmann distribution, hole blocking factors in our equation of motion cause the electronic populations to relax to a Fermi-Dirac distribution. These factors are an old concept, but we show how they can be derived with a combination of time-dependent perturbation theory and the extended normal ordering of Mukherjee and Kutzelnigg. The resulting non-equilibrium kinetic equations generalize the usual Redfield theory to many-electron systems, while ensuring that the orbital occupations remain between zero and one. In numerical applications of our equations, we show that relaxation rates of molecules are not constant because of the blocking effect. Other applications to model atomic chains are also presented which highlight the importance of treating both dephasing and relaxation. Finally we show how the bath localizes the electron density matrix.
A perfect theory of electronic dynamics must relax towards the correct equilibrium distribution of population at long times. However, satisfying this condition is not trivial. The two most common approaches for simulating non-equilibrium electronic dynamics in chemistry, Ehrenfest method and the surface hopping approach, do not satisfy this condition exactly. In the case of Ehrenfest dynamics, the violation of detailed balance is severe\(^1\) and the dynamics can only be taken seriously at short times. In the case of surface hopping, the violation is so small it is hard to identify\(^2\).

Both these methods are usually formulated in a basis of distinguishable (Boltzmannian) electronic states. Because the basis must be limited in practice, predictions in the Boltzmannian picture depend on a choice of adiabatic or quasi-diabatic states. States with fractional orbital occupations are also extremely expensive and difficult to treat in a basis of collective electronic states. To address these problems, we are pursuing relaxation dynamics based on the reduced electron density matrices without wavefunctions.

In the one-electron picture, non-equilibrium Green’s function theories\(^3\)–\(^6\) and Boltzmann transport equations\(^7\),\(^8\) do satisfy detailed balance. Master equations which exchange both electrons and energy between a system and a bath of two-level Fermions have also been recently derived and approach a Fermi-Dirac (FD) distribution\(^9\),\(^10\). However, for spectroscopy the most important bath is undoubtedly the bosonic vibrations of the atoms\(^11\). To our knowledge, it has never been explicitly shown how a bosonic bath drives electrons to their correct equilibrium as presented in this paper. We show how a Pauli-blocking effect slows down relaxation, and dephasing of electrons. The derivation that we use is general and can be applied to electron correlation as well. We also use our new expressions to show that the rate of relaxation for a particle-hole excitation is not constant because of the Pauli-blocking
Ordinary system-bath perturbation theory with a bath of bosons does not tend towards FD populations. The equations do not consider exchange statistics so they approach a canonical equilibrium instead. The goal of this paper is to show how the derivation of ordinary system-bath perturbation theory naturally leads to a FD equilibrium if expectation values are taken correctly with respect to a mixed-state, Fermionic vacuum. The resulting kinetic equations resemble Redfield theory but also depend on the hole density. The derivation we provide here is made possible by a powerful and relatively new concept, the extended normal ordering (ENO) of Mukherjee and Kutzelnigg (MK) and is extensible to higher orders, other couplings and correlated states. A related generalized Wick’s theorem concept was recently developed for Green’s Function-based theories.

The present paper is actually the result of our group applying ab-initio master equations without Fermi-blocking to real molecular systems, and predicting rates which were too large. Tracing back the origin of the discrepancy between our theory and experiments, we realized that previous combinations of electronic structure theory and master equations had missed this detail. For linear response away from a determinant, the blocking effect is irrelevant and so the literature is basically correct. A paper using these new formulas in a useful all-electron dynamics code is an immediate follow up. Electron transport methods based on the density matrix will also benefit from the main results of this paper. Electronic statistics can be easily enforced as long as kinetic rates depend on the density matrix.

A. Detailed balance

The textbook perturbation theory of solids in the thermodynamic limit was slightly incorrect until it was revisited by Hirata and He in 2013. The correction
made by those authors replaces expectation values taken with respect to a pure state with expressions appropriate for finite temperature. The approach of this paper is the same. In the non-interacting case, the population of an electronic state at long times should tend to the Fermi-Dirac (FD) distribution:

\[ \bar{n}_i = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}} \]  

(1)

where \( \beta = (k_B T)^{-1} \), \( \epsilon_i \) is the energy of a one-electron state, and \( \mu \) the chemical potential satisfying \( \sum_i \bar{n}_i = N \), the total number of electrons. We use the bar to indicate that this is an equilibrium quantity, where the number of particles exchanged between any two states are equal so the corresponding populations do not change (the condition of detailed balance).

The purpose of this paper is to derive detailed balance based on a microscopic kinetic model, but let us consider the form that the model should take. It is known that a linear kinetic equation can be easily modified by 'Pauli-blocking' factors \((1 - n_i)\), no bar, to reach detailed balance with the FD distribution. Consider a set of non-negative Markovian transition rates between states \( K_{ij} \) satisfying \( \sum_j K_{ij} = 1 \), and canonical detailed balance \( e^{\beta(\epsilon_j - \epsilon_i)} = K_{ij} / K_{ji} \). The blocking factors close any channel which would disobey exclusion. Inserting FD \( \bar{n}_i \)'s into a kinetic equation of this form:

\[ \frac{d}{dt} n_i = \sum_j K_{ij} (1 - n_i) n_j = \sum_j K_{ij} \eta_i n_j \]  

(2)

one sees the number of particles exchanged between any two states are equal, meaning the FD distribution is stationary. We have introduced \( \eta_i \), the diagonal of the one-hole density matrix. Equation (2) is the form a kinetic equation must take to satisfy Fermionic detailed balance. Exclusion factors are an old concept going all the way
back to Landau\textsuperscript{22}, as an ad-hoc correction to phenomenological equations for electron
transport. They are not only important for population relaxation rates, but also
dephasing rates\textsuperscript{23} which are increasingly relevant to coherent spectroscopy. In a
dephasing process, probability temporarily leaves a state and returns after having its
phase scrambled, but electrons can only visit holes during these events, so dephasing
rate equations are also different for electrons than for particles with distinguishable
Boltzmann statistics\textsuperscript{23}. In the remainder of this paper, we derive an expression
which reduces to Eq. (2) with perturbation theory and also provides a detailed,
improvable microscopic model for dephasing between Fermionic states. It may be
worth mentioning that Eq. (2) resembles a multivariable logistic process \( x_{n+1} =
r(x_n(1-x_n)) \), a sequence famous for its chaotic behavior in the regime where \( r > 3 \),
although our physical rates never approach this regime.

II. FERMIONIC MASTER EQUATION

We begin our derivation with electrons in energetic contact with an infinite number
of bosons at \( T \geq 0 \) equilibrium. To show that FD is the exact equilibrium, they
must be non-interacting, but the correction we derive to the dynamics applies in the
interacting case as well. We will use a notation for second quantization which follows
Ref.\textsuperscript{13}. Summation over repeated indices is implied.

\[
\hat{H} = \hat{H}_e + \hat{H}_b + \hat{V} = \sum_i \epsilon_i a_i^\dagger a_i + \sum_\alpha \omega_\alpha b_\alpha^\dagger b_\alpha + \sum_{\alpha,i,j} V_{i,j,\alpha} a_j^\dagger a_i (b_\alpha^\dagger + b_\alpha) \tag{3}
\]

In the open-systems approach, the Hamiltonian is put into this form after diagonal-
izing the electronic part from some localized basis \( |\nu_i\rangle = \sum_j \hat{U}_{ij} |\nu_j\rangle \) with electronic
coupling. In the original basis, which is the atomic basis in our work, the system-bath
coupling is usually taken to be diagonal: \( (b_\alpha^\dagger + b_\alpha) g_{\alpha,\nu} |\nu\rangle \langle \nu| \), but leads to off-diagonal
coupling: \( V_{i,j,\alpha} = \sum_{\nu} U_{i,\nu} g_{\alpha,\nu} U_{j,\nu}^\dagger \) in system energy eigenbasis used to propagate the dynamics. We discuss how Eq. (3) is prepared atomistically in the section Numerics.

The goal is to obtain an equation of motion for the one-Fermion reduced density matrix: \( \gamma_p^q = \langle a_p a_q \rangle \). Taking the expectation value of the Heisenberg equation for the operator, or perturbative approximations to it, we can obtain equations of motion. However, \( \langle \rangle \) is the expectation value of a one-body operator under an impure state during the dynamics, and eventually \( \gamma_j^i = \delta_j^i \bar{n}_i \). The Wick’s theorem is the usual procedure to obtain expectation values for states that have idempotent densities: \( \gamma^2 = \gamma \), and is appropriate for the initial condition of most electronic dynamics where a single determinant is the ‘reference state’. Using ENO, we can take expectation values using the reduced density matrices of the state as ‘a reference’, whether or not they are impure throughout the relaxation process. Mukherjee and Kutzelnigg hinted at this application in their classic paper.

Similar to MK’s derivation of the multi-configuration self-consistent field gradient with ENO, we would like to derive how the coupling changes the expectation value of a generic one-electron operator without any reference contribution. By definition, that is the ENO part of the perturbative correction to \( \frac{d}{dt} \gamma \). We would also like \( V \) to have vanishing expectation value under the reference so that perturbation is purely time-dependent. Both of these conditions are equivalent to deciding that the operators in our perturbation theory are their MK normal-ordered counterparts. The complete Liouville equation for the density matrix is then the sum of the second-order ENO correction we will derive and reference Liouville equation:

\[
\dot{\gamma} = \frac{i}{\hbar} [\gamma, H_e] + \langle \frac{d}{dt} (a_p^q)^{(2)} \rangle_{ENO}
\]  

(4)

In what follows, all operators are MK normal-ordered with respect to the reference density matrices at the present instant of time (we omit the tildes that MK use in
their paper). When using these formulas to propagate, it is understood that every time increment has its own reference density and its own normal ordering determined by the previous instant. Following the derivation of our previous work using the time-convolutionless perturbation theory of Shibata\textsuperscript{25,26} and assuming a separable initial condition between bosons and electrons, we reach the following interaction picture expression for the second-order correction to dynamics of a one-electron operator:

\[
\frac{d}{dt}(a_q^{(2)}) = \left(\frac{i}{\hbar}\right)^2 \int_0^t dt_1 [[a_q^p, V_{r,s,\alpha}(t_1)(b^\alpha(t_1) + b_\alpha(t_1))]a_s^r, V_{i,u,\alpha}(t)a_u^t(b^\alpha(t) + b_\alpha(t))] 
\]  

(5)

Making the usual Born approximation for a second-order master equation, expectations of the electronic and bosonic operators factorize. The boson expectation value provides a time-dependent factor, and the expectation value of the double-commutator for the electronic operators is where the MK normal-ordering yields something new:

\[
\langle [[a_p^q, a_s^r], a_u^t]\rangle_{\text{ENO}} = \delta_q^r(\gamma_{i u}^t - \eta_{u}^p \gamma_s^t) + \delta_p^s(\gamma_{i u}^t - \eta_{q}^u \gamma_s^t) 
\]  

(6)

This expression says two interesting things. It shows that the expectation value of this double commutator does not depend on the higher-order reduced density matrices regardless of whether they are separable or not. Moreover, even if the reference had strong, two-particle correlations, or it was a double-excitation etc., that does not affect this term\textsuperscript{27}. This result supports the possibility of an accurate dissipative time-dependent Hartree-Fock equation since the dissipation of the one-body density is not coupled to the two-body density through the bath.\textsuperscript{28} Secondly, each factor in this equation of motion depends on the hole-density matrix: \((\eta_{q}^p = \delta_{q}^p - \gamma_{p}^q)\). These are naturally derived Pauli-blocking factors, defined in this equation whether
the density is in a natural orbital basis, or not, for both dephasing and relaxation processes.

We will make several assumptions to incorporate these equations into the form of an ordinary Redfield equation. The first assumption is a Markov approximation ($\lim_{t\to\infty}$), in which the bath remains at Boson equilibrium. This places a constraint on the boson correlation function:

$$\int_0^\infty dt \langle b^\dagger(t)b_\alpha(0) \rangle e^{i\omega_{ij}t} = \Gamma_\alpha(\omega_{ij}) = e^{\beta(\omega_{ij})} \Gamma_\alpha(\omega_{ji})$$  \hspace{1cm} (7)

Which leads to the canonical detailed balance relation in the Redfield equation, but for this equation furnishes canonical K’s like Eq. (2). We introduce a version of $\Gamma$ summed over all $\alpha$ for a given $\nu$ called $\Gamma_\nu$:

$$\frac{d}{dt} \langle (a^a_b)^{(2)} \rangle_{ENO} = \frac{i}{\hbar} 2\Gamma_\nu(\omega_{ef}) V_{ae}^\nu V_{fc}^\nu \gamma_{ie}^c \eta_d^f +$$

$$\left( \Gamma_\nu(\omega_{df}) V_{bc}^\nu V_{fd}^\nu \right)^\dagger \gamma_{ia}^d \eta_e^f - \Gamma_\nu(\omega_{ca}) V_{de}^\nu V_{ac}^\nu \gamma_{ia}^d \eta_b^e -$$

$$\left( \Gamma_\nu(\omega_{db}) V_{ce}^\nu V_{bd}^\nu \right)^\dagger \gamma_{ia}^d \eta_e^f$$  \hspace{1cm} (8)

We note an interesting duality between the electron and the hole in this expression. The third and fourth terms are particle relaxing, but their blocking factors resemble hole-dephasing terms (they couple to only one index of $\eta$), whereas the first and second are particle dephasing, but resemble hole-relaxing terms. A secular approximation must be made to reach an equation which preserves trace, eliminating terms where the frequencies of the oscillating interaction picture factors do not cancel. The
resulting electronic equation of motion is the key result of our paper:

\[ \dot{\gamma}_a^a = \frac{i}{\hbar} (\gamma_k^a \epsilon_k - \epsilon_k \gamma_k^a) + \left( \frac{i}{\hbar} \right)^2 \{ \delta(\omega_{af} - \omega_{fc}) \Gamma_{\nu}(\omega_{cf}) V_{ae}^{\nu} V_{fc}^{\nu} \gamma_{b}^c \eta_{e}^f + \delta(\omega_{bf} - \omega_{fd})(\Gamma_{\nu}(\omega_{df}) V_{be}^{\nu} V_{fd}^{\nu}) \uparrow \gamma_{d}^a \eta_{f}^e - \delta(\omega_{db} - \omega_{ac}) \Gamma_{\nu}(\omega_{ca}) V_{de}^{\nu} V_{ac}^{\nu} \gamma_{b}^c \eta_{e}^f - \delta(\omega_{ca} - \omega_{bd})(\Gamma_{\nu}(\omega_{db}) V_{ce}^{\nu} V_{bd}^{\nu}) \uparrow \gamma_{d}^a \eta_{e}^f \} \]

where \( \omega_{mn} = \epsilon_m - \epsilon_n \). Which is similar to the form of a secular Redfield equation but with blocking factors. This equation rigorously preserves the trace of the one electron reduced density matrix and equilibrates to FD. In the case that the density starts without coherence, \( \eta \) is diagonal and the equation takes the form of Eq. (2). We will now discuss the importance of these blocking factors in the evolution of populations and coherences using calculations on model systems.

III. RESULTS

First we will demonstrate that propagation of Eq. (9) reproduces Fermi-Dirac statistics. To produce a model with the form of Eq. (3), we consider a Huckel model of atomic sites. Each site has an energy \( E_{\nu} = 1.0 \text{ au} \) and is coupled to its nearest neighbors with a coupling strength \( \hat{V}_{e,\nu} \). The energy of each site fluctuates due to the system-bath coupling, and the spectrum of these fluctuations is determined by a spectral density for this site \( J_{\nu}(\omega) = \sum_{\alpha} \frac{\hbar^2}{2} (\omega_{\alpha})^2 g_{\nu,\alpha}^2 \delta(\omega - \omega_{\alpha}) \) of the Drude-Lorentz form. We have previously shown a method to obtain these spectral densities atomistically from limited amounts of molecular dynamics, but in this work we assume a strong, high-frequency bath\(^{29}\) to test positivity and rapidly achieve relaxation. After assigning a spectral density and coupling in the real-space \( \nu \) basis, the electronic Hamiltonian is diagonalized to recover a Hamiltonian of the form (3). Some of the dynamics is performed at a very high temperature so that the exact reproduction of
FIG. 1: A linear tight binding chain with 12 sites, half-filled with 6 electrons, initially at infinite temperature, in which populations of all states are equal, approaches a FD distribution at 500 K in the long time limit ($\hat{V}^{e}_{\nu,\nu} = 0.005$ au). Solid lines denote the energy eigenstates; dashed lines denote the FD population of the corresponding energy eigenstate at this chemical potential.

FD-statistics is made clear. However, blocking has important effects even at room temperature; we show some dynamics results at 300K to this effect. In all cases we half-fill the chain with electrons, and the chemical potential of the system is constant as per Eq. (3).

The electronic dynamics resulting from Eq. (9) preserves the trace of the electronic density matrix and produces a FD distribution at long times. Experiments with several different coherent and incoherent initial conditions and a very strong bath all equilibrate to a FD distribution (Fig. 1). Solutions of the ordinary secular Redfield equation are exponential with time constants determined by the eigenvalues of $K_{ij}$; however, our trajectories with Fermi blocking do not take the same form. There are direct implications for the kinetics of excited state relaxation, and the interpretation of transient absorption spectra which are ordinarily fit to a superposition of decaying exponentials. Because of Fermi-blocking, particle-hole excitations and especially multiple particle-hole excitations do not relax with simple exponential
FIG. 2: An 8-site, 4-electron model is initialized in a particle-hole state (HOMO-2 →LUMO-2), and allowed to relax at 300 K ($V^{e}_{\nu,\nu} = 0.05$ au). (a) Energy eigenstate populations as functions of time. (b) The rate (right scale) at which the model returns to the many-electron ground state (population of g.s. on the left scale) is not constant as a function of time due to blocking effects.

kinetics. We define a ground-state probability based on the overlap of the T=0 K ground state and the density during the dynamics: $P_g(t) = \prod_i (1-|n_i(t) - \Theta(\epsilon_i - \mu)|)$, where $\Theta$ is the step function. Here we simulate an 8-site chain at T=300 K, with otherwise unchanged parameters. We initialize the density in a particle-hole excited state by unfilling HOMO-2 and filling HOMO+2 and monitor $P_g(t)$ to observe the time dependence of the relaxation rates (Fig. 2). For single particle-hole states, the rate of relaxation begins rapid as electrons fill in holes (Fig. 2) and then adopts a slower ‘blocked’ and essentially exponential relaxation rate dominated by LUMO→HOMO relaxation at long times. The effective rate only varies by roughly a factor of ten because of the blocking effect. Consequently, it would be difficult to separate from other possible rate fluctuations in ultrafast spectroscopic experiments although we predict that it exists.

Off-diagonal elements of a density matrix are called coherences, and their decay is called dephasing. As has been recently reported by other authors, the dephasing rate of Fermions is considerably different from what ordinary Redfield theory would
predict\textsuperscript{23}. In distinguishable models of electronic relaxation, coherence tends to be an ambiguous quantity because it is dependent on the chosen basis. In both the energy eigenbasis, and the position eigenbasis coherence has important and measurable implications. In the former, coherence should be zero in the thermodynamic limit. When they are nonzero, energy-basis coherences oscillate. Our kinetic model does completely decay these coherences and also shows why an atomistic and improvable model for their decay is so important. If we initialize electrons on the left of our chain to reach detailed balance, they naturally flow to the right (Fig. 3). However if only populations are allowed to relax, even though the populations of energy eigenstates rapidly reach a perfect FD distribution, the undecayed coherences lead to unphysical oscillatory currents in the system.

In the position eigenbasis, coherences determine the measurable quantum delocalization of particles. Real-space coherence also limits the efficiency of electronic structure theory, since the cost of calculating exchange energy is completely determined by how slowly the real-space density matrix decays away from the diagonal. With our new theory, we can predict how dynamics and finite temperature effects can lead to the long-range decay of the off-diagonal elements of the electronic density matrix (Fig. 4). This locality can potentially be exploited to make electronic structure models more efficient. Although kinetic equation (2) is non-linear in the density matrix, in our experience it faithfully maps any density matrix to FD equilibrium at long times, as it should since FD density is a known solution of Eq. (9). We have not proven that FD is the only possible solution, but we strongly suspect it is.

IV. DISCUSSION AND CONCLUSIONS

Fermionic relaxation rates must depend nonlinearly on the density matrix to be correct at long times. Consequently, relaxation rates for Fermionic states are not con-
FIG. 3: The atom-basis populations of two trajectories at 5000 K ($\hat{V}_e^{\nu,\nu} = 0.05$ au) (a) without dephasing and (b) with dephasing, showing the importance of dephasing in electronic dynamics. In both cases, the initial condition is half-filling with all electrons forced to the left of the chain. The populations in the energy eigenbasis of these trajectories are rigorously FD at final time (the bottom of the plot). Without dephasing (a) electron currents do not decay, whereas with all the terms in Eq. (9) (b) they rapidly decay and all electronic motion is halted by dissipation to the bath after the initial relaxation. Dephasing is as important to accurate electronic dynamics as population kinetics.

FIG. 4: A 32-atom chain is initialized into its ground state ($\hat{V}_e^{\nu,\nu} = 0.05$ au), and allowed to warm in contact with a 5000 K bath. $-1/\log\{\gamma(x,x')\}$ at two different times are plotted at the same scale to make the coherence decay visible.
stant as a function of time, and tend to slow down over the course of non-radiative relaxation. This effect is extremely unclear in a Boltzmannian ‘exciton’ model. Hole blocking makes rates of electronic relaxation and dephasing slower than the corresponding rates for distinguishable particles.

These are second-order equations. The rates of transition they predict will become inaccurate in the strong coupling limit, even though we obtain FD with very strong couplings. The main feature of these equations is that they are systematically improvable. One can easily ‘Fermi-block’ surface hopping rates and perform surface hopping for individual electrons. The results of this paper suggest that with Fermi blocking surface hopping for electrons would, for all intents and purposes, tend to FD. However, that electronic surface hopping would beg for a systematically improvable path to dephasing rates, like its Boltzmann counterpart.

We have found that the MK normal-ordering is an especially useful technique for dynamics, allowing us to work around the impurity of the state. We used it to provide an promising equation of motion for electrons and simulate non-equilibrium vibronic relaxation. As in our previous work, the perturbation theory could also be used to develop electronic equations of motion that treat electron correlation effects, although that will require an automated version of ENO algebra. This paper opens the door to answering whether interacting equilibrium differs meaningfully from the FD equilibrium in real materials, and how that equilibrium is approached. Extension of this work towards higher electronic density matrices is ongoing in our laboratory.

It is significant that these equations approach Fermionic detailed balance naturally, as opposed to enforcing detailed balance in an ad-hoc way. In a related vein, sometimes Pauli-blocking factors are taken to be $\bar{\eta}_i$ instead of $\eta_i(t)$, which is correct at equilibrium. However, this results in slightly different, and based on the derivation of this work, slightly incorrect kinetics that would not capture the time-dependence of the blocking effect. Applications of this work to predict rates of non-radiative
relaxation in molecules is an active pursuit in our laboratory.

V. ACKNOWLEDGEMENTS

We thank The University of Notre Dame’s College of Science and Department of Chemistry and Biochemistry for generous start-up funding and Honeywell Corporation. T. S. N. gratefully acknowledges the support of the NSF Graduate Research Fellowship under grant 1313583. We acknowledge valuable conversations with Liviu Nicolaescu (Notre Dame), Geoff Thompson (Iowa State), Jarrod McClean, Samuel Blau, and Thomas Markovich (Harvard).

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See MK’s paper for details.

The two-body density does couple to the one-body density via the Coulomb interaction in an atomistic Hamiltonian.

Four Drude-Lorentz functions are chosen with widths, amplitudes and central frequencies of the following form (au): \{(0.0001, 0.00001, 0.0001), (0.001, 0.0017, 0.0017), (0.013, 0.023, 0.027), (0.01, 0.017, 0.017)\}. 