Gauge Theory for the Rate Equations: Electrodynamics on a Network

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Systems of coupled rate equations are ubiquitous in many areas of science, for example, in the description of electronic transport through quantum dots and molecules. They can be understood as a continuity equation expressing the conservation of probability. It is shown that this conservation law can be implemented by constructing a gauge theory akin to classical electrodynamics on the network of possible states described by the rate equations. The properties of this gauge theory are analyzed. It turns out that the network is maximally connected with respect to the electromagnetic fields even if the allowed transitions form a sparse network. It is found that the numbers of degrees of freedom of the electric and magnetic fields are equal. The results shed light on the structure of classical Abelian gauge theory beyond the particular motivation in terms of rate equations.

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Introduction.—Let us consider a system that assumes states $|i\rangle$ with probabilities P_i, where the states form a finite or countable set. The probabilities must add up to unity, $\sum_i P_i = 1$. If the rates of change of the probabilities are linear functions of the probabilities, we can write

$$\dot{P}_i = \sum_j (R_{ij} P_j - R_{ji} P_i). \tag{1}$$

This is a set of rate equations, containing the transition rates R_{ij} from state $|j\rangle$ to state $|i\rangle$. The first term under the sum describes transitions from other states to $|i\rangle$, whereas the second describes transitions out of state $|i\rangle$. Often, many of the R_{ij} are zero. Importantly, Eq. (1) conserves probability: $\sum_i \dot{P}_i = 0$.

Rate equations are ubiquitous in science, in particular, in physics, chemistry, and biology. They describe systems far from equilibrium, such as lasers [1], semiconductor devices [2], quantum dots [3], chemical reactions [4], enzyme kinetics [5], and biological populations [6].

As a specific example, we discuss a molecular quantum dot coupled to leads. The time evolution of the complete system of molecule and leads is described by the von Neumann equation for the full density operator, $\dot{\rho} = -i[H, \rho]$, where H is the Hamiltonian of the complete system and $\hbar = 1$. If one is interested in the properties of the molecule, it is advantageous to integrate out the states of the leads to obtain an equation of motion (master equation) for the reduced density matrix ρ^d in the many-particle Hilbert space of the molecule alone [7–18]. This requires approximations. For example, if the tunneling amplitude between the molecule and leads is small compared to the typical molecular energy-level spacing, one can apply perturbation theory [10,12–18]. The master equation contains diagonal and off-diagonal components of ρ^d. If one assumes that the off-diagonal components, i.e., the superpositions, decay rapidly on the relevant time scale [19], one is left with coupled rate Eqs. (1) for the diagonal components, which are just the probabilities $P_i \equiv \rho^d_{ii}$ of molecular many-body states.

Our discussion is not specific to a particular incarnation of the rate equations. Rather, it starts from the general principle of conservation of probability. We consider the *network* formed by the states $|i\rangle$. The transitions between them are the edges of this network. The rate Eqs. (1) can be written as a *continuity equation* on the network [20],

$$\dot{P}_i = \sum_j J_{ij}, \tag{2}$$

where J_{ij} is a probability current defined as an antisymmetric quantity on the edges [21],

$$J_{ij} \equiv R_{ij} P_j - R_{ji} P_i. \tag{3}$$

The conservation law (2) suggests to look for a gauge theory that implements it [22]. The field suggests a generalization of electrodynamics.

There is a sizable literature on electrodynamics [23–26] and non-Abelian gauge theories [27–29] on regular lattices, mainly motivated by discretizing continuum theories to facilitate numerical calculations. Chew [24] introduces a discrete vector calculus to formulate electrodynamics on a lattice. A Lagrangian approach has been used to obtain a network approximation for electrodynamics in certain electronic devices [30]. An electronic-network model for coupled linear chemical reactions has also been proposed [31]. In this model, concentrations and not probabilities are mapped onto charges and a magnetic field or gauge fields are not introduced.

The present Letter can also be read as a generalization of classical electrodynamics to a network and is thus of interest for the fundamental understanding of gauge theories, independently of the motivation from rate equations. It is not obvious how one should generalize Chew's discrete vector calculus [24] to a network, since there are no natural definitions of forward and backward differences. Maxwell equations in integral form are more easily generalized. For example, the electric flux through a "wall" that divides the network into two parts is a meaningful quantity. It turns out that due to the lack of a length scale the electric (magnetic) field is the same as the electric (magnetic) flux and there is no difference between the differential and integral forms of the Maxwell equations.

Maxwell equations.—Our goal is to construct electric and magnetic fields that implement the conservation of probability. If we view P_i as a charge density, it should provide the sources of the electric field. We define an antisymmetric field E_{ij} on the edges. Then Gauss' Law should read

$$\sum_j E_{ji} = P_i. \tag{4}$$

The sum over all outgoing electric fields equals the enclosed charge. Note that E_{ji} is generally nonzero also if transitions from $|i\rangle$ to $|j\rangle$ are forbidden so that $J_{ji} = 0$. This is not surprising since in standard electrodynamics there is certainly an electric field in an insulator. As far as the electric (and, as we will see, also the magnetic) field is concerned, the network is maximally connected, every node is the neighbor of every other node.

Equation (4) leads to a problem: Summing over i we find

$$0 = \sum_{ij} E_{ji} = \sum_i P_i \stackrel{?}{=} 1. \tag{5}$$

We can rectify this by adding an additional fictitious node 0 with $P_0 = -1$ and $R_{i0} = R_{0i} = 0$ for all i. Node 0 does not affect the rate equations for the real states but makes the network charge neutral. The problem is that in Eq. (5) we obtain a relation between the flux through the surface of the system and its total charge. However, our network does not have a surface. The same problem arises if one tries to construct electrodynamics on any compact space.

Next, we define a magnetic field $B_{(ijk)}$ on the elementary oriented plaquettes of the network, which are oriented triangles (ijk). The magnetic field is invariant under cyclic commutation of i, j, k and changes sign for anticyclic commutations. To have J_{ij} generate the magnetic field, we write the Ampère-Maxwell Law as

$$\sum_k B_{(ijk)} - \frac{1}{c}\dot{E}_{ji} = \frac{1}{c} J_{ji}. \tag{6}$$

Figure 1(a) shows that the equation contains a sum over the magnetic field penetrating all plaquettes adjacent to the edge carrying the current, corresponding to a line integral. E_{ji} and $B_{(ijk)}$ have the same dimension. Then c is a frequency, not a velocity, since the network does not have a length scale.

Faraday's Law should relate the time derivative of the magnetic field through a plaquette to the sum over electric fields along its edges. This is achieved by

$$E_{ji} + E_{kj} + E_{ik} + \frac{1}{c}\dot{B}_{(ijk)} = 0. \tag{7}$$

The sum $E_{ji} + E_{kj} + E_{ik}$ is the analogue of the electromotive force around the plaquette so that its inductance is $1/c$.

Finally, the magnetic flux through the surface of any volume should vanish. An elementary cell on the network can be characterized by four nodes i, j, k, l. Then,

$$B_{(ijk)} + B_{(jlk)} + B_{(lik)} + B_{(ilj)} = 0. \tag{8}$$

Figure 1(b) shows that the orientation of all faces is the same.

The Maxwell equations imply the continuity equation: Summation of Eq. (6) over j gives

$$\sum_{jk} B_{(ijk)} - \frac{1}{c}\sum_j \dot{E}_{ji} = \frac{1}{c}\sum_j J_{ji}. \tag{9}$$

The first term vanishes by symmetry. Using Eq. (4) we reobtain Eq. (2). Note that this derivation also works if the rates R_{ij} depend on time. In fact, the derivation does not make any assumption about the dependence of J_{ij} on P_i.

Coulomb and Biot-Savart Laws.—We now consider the solution of the Maxwell equations for the fields. Direct calculation yields $P_i - P_j = NE_{ji} + c^{-1}\sum_k \dot{B}_{(ijk)} = NE_{ji} + c^{-2}\ddot{E}_{ji} + c^{-2}\dot{J}_{ji}$. Here, N is the number of nodes, including node 0. In the static case, we thus find the Coulomb Law

$$E_{ji} = \frac{1}{N}(P_i - P_j). \tag{10}$$

Interestingly, it is local: The static electric field on an edge is completely determined by the charges on the adjacent nodes.

We also find $c^{-1}(J_{ji} + J_{kj} + J_{ik}) = NB_{(ijk)} + c^{-2}\ddot{B}_{(ijk)}$. In the static limit we obtain a local Biot-Savart Law

$$B_{(ijk)} = \frac{1}{cN}(J_{ji} + J_{kj} + J_{ik}). \tag{11}$$

Gauge fields.—As in standard electrodynamics, we introduce gauge fields to satisfy the homogeneous Maxwell Eqs. (7) and (8). The magnetic field is written as

$$B_{(ijk)} = A_{ji} + A_{kj} + A_{ik}, \tag{12}$$

where A_{ij} is antisymmetric. The form on the right-hand side is analogous to a curl, compare Eq. (7). Interestingly, the magnetic field has many more components than the "vector potential" A_{ji}, which is defined on edges, not plaquettes.

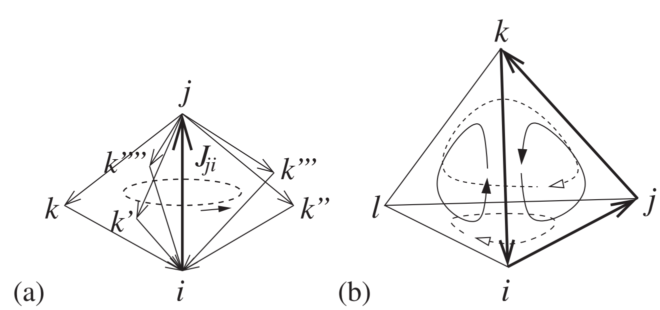

FIG. 1. (a) Sketch showing that the Ampère-Maxwell Law relates the current on the edge from i to j to the circulation of the magnetic field around this edge. (b) Sketch of an elementary cell on the network, bounded by four plaquettes oriented outwards.

Then Faraday's Law takes on the form $E_{ji} + \dot{A}_{ji}/c + E_{kj} + \dot{A}_{kj}/c + E_{ik} + \dot{A}_{ik}/c = 0$, which suggests to write

$$E_{ji} = -(\phi_j - \phi_i) - \frac{1}{c}\dot{A}_{ji}, \tag{13}$$

where the "scalar potential" ϕ_i is defined on the nodes. It is easy to show that Eqs. (7) and (8) are indeed satisfied.

The electric and magnetic fields are invariant under the simultaneous gauge transformations

$$A_{ji} \to A_{ji} + \Lambda_j - \Lambda_i, \tag{14}$$

$$\phi_i \to \phi_i - \frac{1}{c}\dot{\Lambda}_i, \tag{15}$$

where Λ_i are arbitrary time-dependent functions. One can now consider specific gauge choices. For example, the analogue of the Lorentz gauge requires

$$\sum_j A_{ji} + \dot{\phi}_i = 0, \qquad \sum_i \phi_i = 0. \tag{16}$$

It is easy to show that this choice is possible. Then the remaining two Maxwell equations take on the simple form

$$N\phi_i + \frac{1}{c^2}\ddot{\phi}_i = P_i, \qquad NA_{ji} + \frac{1}{c^2}\ddot{A}_{ji} = \frac{1}{c}J_{ji}. \tag{17}$$

These equations are coupled by the gauge condition (16).

The representation in terms of gauge fields facilitates the discussion of the number of dynamic degrees of freedom. For a regular lattice, He and Teixeira [26] show that the electric and magnetic fields contain the same number of independent degrees of freedom. For the network, we first reformulate the question by asking how many electric and magnetic field components can consistently and independently be specified.

We choose the gauge $\phi_i = 0$ so that the $A_{ij}(t)$ are $N(N-1)/2$ independent functions. Since the Maxwell equations lead to second-order differential equations for the $A_{ij}(t)$, we can and must specify two initial conditions for each to determine the solution. This gives $N(N-1)$ independent degrees of freedom. If we specify the initial values for the electric and magnetic fields instead, we must specify all $N(N-1)/2$ components of E_{ij} to fix $\dot{A}_{ij}$. We then must also specify $N(N-1)/2$ components of $B_{(ijk)}$ to determine the solution. Thus the number of dynamic degrees of freedom in the electric and magnetic field is the same also on the network.

Lagrangian and energy.—The Maxwell equations can be concisely expresses by the Lagrangian

$$L = \frac{1}{2}\sum_{\langle ij\rangle} E_{ij}^2 - \frac{1}{2}\sum_{(ijk)} B_{(ijk)}^2 - \sum_i P_i\phi_i + \frac{1}{c}\sum_{\langle ij\rangle} J_{ij}A_{ij}. \tag{18}$$

As usual, E_{ij} and $B_{(ijk)}$ are to be expressed in terms of the gauge fields. The sum $\sum_{\langle ij\rangle}$ is over all edges, counting each edge once, and $\sum_{(ijk)}$ is over all elementary plaquettes, counting each plaquette once. The action is $\mathcal{S} = \int dt L$. It is straightforward to show that the Euler-Lagrange equations for Hamilton's principle $\delta S = 0$ reproduce the two inhomogeneous Maxwell equations. Incidentally, a covariant formulation is not possible due to the different structure of space (network) and time (continuum).

The Lagrangian suggests to define the energy densities of the electric and magnetic fields as $w_{ji}^{\mathrm{el}} \equiv E_{ji}^2/2$ and $w_{(ijk)}^{\mathrm{mag}} \equiv B_{(ijk)}^2/2$, respectively. The local energy balance can then be expressed using the "Poynting vector" $S_{ji}^k \equiv -cE_{ji}B_{(ijk)}$. With this definition we obtain

$$\frac{d}{dt}w_{ji}^{\mathrm{el}} = -\sum_k S_{ji}^k - E_{ji}J_{ji}, \tag{19}$$

$$\frac{d}{dt}w_{(ijk)}^{\mathrm{mag}} = -S_{ji}^k - S_{kj}^i - S_{ik}^j. \tag{20}$$

Energy is not conserved but changes due to Ohmic dissipation. However, unlike in standard electrodynamics, the energy can actually increase, since $E_{ji}J_{ji}$ can be negative for asymmetric rates R_{ij}. Note that the generalization of the cross product yields a peculiar object S_{ji}^k, which is symmetric only in its two lower indices.

Medium equation.—The Maxwell equations do not yet form a closed set. As in standard electrodynamics in media one has to complement the Maxwell equations by medium equations describing the response of the medium.

The situation most closely resembling our case is that of a conductor. Ohm's Law for the network would read $J_{ij} = \sigma_{ij}E_{ij}$. However, in our case the medium equation is just the definition of the current, Eq. (3). This equation is conceptually different from Ohm's Law in that it expresses the current density in terms of the charges, not the electric field. The origin is that we are actually describing a diffusive system.

We *can* rewrite the medium equation to resemble Ohm's Law: With Gauss' Law (4) we obtain

$$J_{ji} = \sum_k (R_{ji}E_{ki} + R_{ij}E_{jk}). \tag{21}$$

This is a *nonlocal* version of Ohm's Law on the network, where the rates R_{ij} play the role of conductivities. However, since R_{ij} is not symmetric, nonzero currents can be present in the stationary state.

If the rates are symmetric, $R_{ij} = R_{ji}$, which is a sufficient but not necessary condition for detailed balance [20], we can rewrite the medium equation as

$$J_{ji} = NR_{ji}\left(E_{ji} + \frac{1}{cN}\sum_k \dot{B}_{(ijk)}\right). \tag{22}$$

Here, NR_{ji} acts as the conductivity and the expression in parentheses is the force per unit charge. The first term is the normal electric field, while the second is not present in standard electrodynamics. It is the rate of change of magnetic circulation around the edge from j to i.

Discussion and conclusions.—We have formulated classical electrodynamics on a network of possible states, motivated by the conservation of probability in systems of coupled rate equations. We close with a number of remarks.

(i) Even if the transition rates are nonzero only between certain states i, j, we have to introduce electromagnetic fields on *all* possible edges $\langle ij \rangle$ and plaquettes (ijk) of the network. Thus this system does not reduce to electrodynamics on a lattice [24] for the case that the nodes connected by allowed transitions form a regular lattice. Nevertheless, the number of degrees of freedom of the electric and magnetic fields on the network are equal, as for a regular lattice.

(ii) As in standard electrodynamics, only the two inhomogeneous Maxwell equations are required to implement the continuity equation. Thus the theory allows to introduce magnetic monopoles, which here live on the dual network formed by the cells of the original network.

(iii) Compared to continuum electrodynamics, scalar fields correspond to quantities defined at the nodes (P_i, ϕ_i), polar-vector fields correspond to quantities defined on edges (J_{ij}, E_{ij}, A_{ij}), and axial-vector fields correspond to plaquette fields ($B_{(ijk)}$). A Poynting vector can be defined, but has a more complicated structure than the "vector" E_{ij} because electric and magnetic fields live in different places.

(iv) We have reformulated the rate equations as a variational principle, $\delta S = 0$, for the action of electromagnetic fields. What is gained by this formulation? On the one hand, it represents a new way to think about rate equations within the framework of electrodynamics. It works for *any* dependence of the current on the probabilities and their time derivatives, as long as J_{ij} is antisymmetric.

The framework is expected to be useful for inverse problems: How can one construct a dynamical system with specified properties? As an example, note that the new fields $E'_{ji} \equiv E_{ji} + \sum_k \dot{B}_{(ijk)}/cN$, $B'_{(ijk)} \equiv 0$ and the new current $J'_{ji} \equiv J_{ji} - c\sum_k B_{(ijk)} - \sum_k \ddot{B}_{(ijk)}/cN$ satisfy the Maxwell equations with the original charges P_i. Since $B' = 0$, $J'_{ji} + J'_{kj} + J'_{ik}$ vanishes for all i, j, k, cf. the discussion leading to Eq. (11). This means that for any time-dependent probabilities P_i one can find a dynamical system with these probabilities and with $J_{ji} + J_{kj} + J_{ik} = 0$. Since the current is curlless, one can write it in terms of a "current potential," $J_{ji} = -(\psi_j - \psi_i)$. Gauss' Law then shows that $\psi_i = -\dot{P}_i/N$ is a solution.

(v) The framework is of interest beyond the motivation in terms of rate equations, since it shows that a classical gauge theory can be formulated consistently on a network, which does not have a natural metric. For this reason the parameter c is a frequency instead of a velocity. It is an interesting question how non-Abelian gauge theories fare in this context.

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