Generalized Method for Charge Transfer Equilibration in Reactive Molecular Dynamics

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Abstract

Variable charge models (e.g., EEM, QEq, ES+) in reactive molecular dynamics simulations often inherently impose a global charge transfer between the atoms, approximating each system as ideal metal. Consequently, certain surface processes (e.g., adsorption, desorption, deposition, sputtering) are affected, leading to dubious dynamics. Among others, the QTPIE model addresses this issue, while at the same approximating each system as an ideal insulator. In this work, the respective demand for a continuous description is met by the charge transfer equilibration or QTE model. This method is derived from scaled charge transfer variables which are solved for, instead of considering atomic charge variables. The latter, however, are in the end obtained by a respective transformation, employing an extended Lagrangian method. QTE may serve as alternative to ACKS2, which to the best of the authors’ knowledge represents the state of the art for variable charge models. We moreover propose a mirror boundary condition and its implementation to accelerate surface investigations. The models proposed in this work facilitate reactive molecular dynamics simulations which describe various materials and surface phenomena appropriately, while at the same time reducing the computational effort.
I. INTRODUCTION

Molecular dynamics can be subdivided into three groups, i.e., classical, reactive and ab initio molecular dynamics. The former is commonly used to investigate simple processes on larger length and time scales. The latter allows for the thorough study of complex material compositions and dynamics at the cost of substantially higher computational resources. The gap between these two methods is addressed by reactive molecular dynamics (RMD), which typically employ the concept of bond order in combination with variable (or fluctuating) charge methods. The bond order of an atom is used to describe its environment dependent interatomic bond strength. Variable charge models allow for a corresponding environment dependent charge distribution. The latter is determined by fulfilling Sanderson’s electronegativity equalization (EE) within the system [1]. This corresponds to the minimization of the overall electrostatic energy under the constraint of charge neutrality and a fixed atom geometry [2]. Some of the most prominent self-consistent variable charge models are the electronegativity equalization method (EEM) [3–6], charge equilibration (QEq) [7] and electrostatic plus (ES+) [8]. Apart from parameter definitions, they differ from each other in the way the atomic charge is spatially distributed (in QEq, the hydrogen electronegativity is also meant to be charge-dependent). In EEM, point charges and eventually a shielded Coulomb potential are used to model electrostatic interactions [9]. In QEq, a single normalized ns Slater orbital is used to describe the outer valence orbital. Furthermore, the diatomic Coulomb integral is evaluated. ES+ extends the QEq model by additional consideration of the core charge. Hence, RMD potentials (e.g., ReaxFF [10, 11] and COMB3 [12]) that make use of both concepts (bond order and variable charge) enable simulations of particular complex material compositions or phenomena.

The bidirectional transition from one system to two or more non-bonded systems (e.g., dissociation, recombination, desorption, adsorption, sputtering, deposition, fragmentation) as well as the interaction of the latter with each other (e.g., two or more distant molecules) cause issues when applying EEM, QEq or ES+. All models allow for a non-physical charge transfer between spatially separated atoms, molecules and solids [11]. The electronegativity is equalized within the total system, without any geometrical limitations. This corresponds to a global charge transfer between all atoms until the EE is reached. Even a single system is therefore always approximated as an ideal conductor (metal) [13, 14]. However, manifold
RMD studies of insulators, where either EEM, QEq or ES+ was applied, have proven that at least this circumstance can be dealt with by the respective RMD formalism. The metallic approximation eventually causes issues though, when the polarization due to an external electric field is important (e.g., resistive switching mechanisms) [15].

This methodical challenge has been addressed using an explicit consideration by applying an extended Lagrangian method and a few more recently published charge models. For the said Langrangian method, it was proposed to split up the system into subsystems (e.g., molecules) and solve for the EE only within those (allowing for intramolecular, but omitting intermolecular charge transfer) [16]. The drawback of this approach is inherently the inability of describing any bidirectional transition between those systems (e.g., dissociation, recombination).

The split charge equilibration (SQE) method is based on EEM, but makes use of diatomic charge transfer instead of atomic charge variables [17, 18]. While this formalism enables a straightforward way to mitigate long range charge transfer and overall adjust it more precisely, it also increases substantially the number of charge-related variables and thus computational cost. The atom-condensed Kohn-Sham density functional theory approximated to second order (ACKS2) model is a generalization of SQE, while, however, employing atomic charge variables [19, 20]. ACKS2 is based on a sophisticated derivation (no global charge transfer) and to the best of our knowledge, corresponds to the state of the art for variable charge models. Recently, it replaced EEM in the ReaxFF potential, but for example yet needs to be implemented in the widely used open-source molecular dynamics simulation framework LAMMPS [11, 21].

For the charge transfer polarization current equalization (QTPIE) method, initially, charge transfer variables were also made use of. In addition, diatomic electronegativity differences (for neutral atoms) were scaled with the ns-type overlap integral to constrain the charge transfer spatially [14, 22, 23]. QTPIE is a generalization of QEq. Later, the charge transfer variables were transformed back to atom charge variables and as a final result, effective electronegativities were defined. The latter can be thought of as being a weighted average of the beforehand mentioned scaled difference. Apart from that QTPIE corresponds to QEq. In the frame of the QTPIE method, all systems are approximated as ideal insulators [14]. Thus, the QTPIE method is not suited for the simulation of metals or semiconductors.

The comparison of QEq with QTPIE leads to the representation via two models, which
can be interpreted as describing the systems in two limiting cases. In QEq (EEM, ES+), any system is approximated as an ideal conductor (metal) with global charge transfer. In QTPIE, any system is approximated as an ideal insulator. In this work, a charge transfer equilibration (QTE) model is proposed, that addresses the gap between these two limiting cases. QTE is therefore an alternative to ACKS2, which is based on a different approach. In addition, a minor extension to the still widely used EEM, QEq and ES+ is described, which allows for a better charge transfer in case of specific surface processes (i.e., adsorption, desorption). Subsequently, a mirror boundary condition results, which accelerates RMD simulations that employ variable charge models. Finally, recommendations for the respective implementations are provided and a final discussion is presented.

II. REVIEW OF VARIABLE CHARGE MODELS

In the following, EEM [3–6], QEq [7], ES+ [8] and QTPIE [14, 22, 23] will be briefly summarized. All of which lead to a set of coupled linear equations, which can be solved in different ways. Here, an extended Lagrangian method for treating fictitious degrees of freedom (atomic charge space) was chosen, as proposed elsewhere [16]. On the one hand, this approach is utilized by a frequently used RMD potential (COMB3) [12]. On the other hand, we believe, that this method allows for a more intuitive interpretation of the respective model. ACKS2 and SQE are not revisited, since their approaches differ immensely and, therefore, do not provide further insight in this context.

A. Extended Lagrangian method for EEM, QEq and ES+

Apart from parameter definitions, EEM, QEq and ES+ differ in the way the atomic net charge is spatially described. The respective electrostatic interaction $J_{ij}$ (hardness in case of $i = j$) between atom $i$ and atom $j$ is therefore different. The electronegativity $\chi_i^0$ for a neutral atom $i$ is, however, consistent throughout these models. Thus, as long as it is not necessary to specify $J_{ij}$, all models can be discussed at once.

The overall goal, which is the determination of the atomic charge distribution $q_i$, is accomplished by the EE. The electronegativity of the $i$-th atom $\chi_i$ can be described by the negated
chemical potential of the electrons $\mu_i$ surrounding their nucleus $i$,
\[
\chi_i = -\mu_i = -\frac{\partial E}{\partial N_e} = e\frac{\partial E}{\partial q_i}
\] (1a)
\[
\tilde{\chi}_i = \tilde{\chi}^0_i + \sum_{j=1}^N J_{ij}q_j
\] (1b)

where $E$ is the total energy of the system, $N_e$ is the number of electrons, $\tilde{\chi}_i = \frac{1}{e}\chi_i$ and $\tilde{\chi}^0_i = \frac{1}{e}\chi^0_i$ [2]. The respective Lagrangian is defined by
\[
\mathcal{L} = \sum_{i=1}^N \frac{1}{2}m_i\dot{r}_i^2 + \sum_{i=1}^N \frac{1}{2}m_q\dot{q}_i^2 + -U[\{q\}, \{r\}] - \lambda \sum_{i=1}^N q_i,
\] (2)

where $U$ is the potential energy of the system, $N$ is the number of atoms, $r_i$ is the nuclei site, $m_i$ is the atom mass, $m_q$ is the fictitious charge mass and $\lambda$ is the Lagrange multiplier. Indexed and plain bold letters indicate vectors and tensors of the complete system space, respectively. The Lagrange multiplier is meant to enforce charge neutrality $\sum_{i=1}^N q_i = 0$.

Newton’s equation of motion for the nuclei are governed by
\[
m_i\ddot{r}_i = -\nabla_i U.
\] (3)

The time evolution of the atomic charge distribution is described by
\[
m_q\ddot{q}_i = -\lambda - \frac{\partial U}{\partial q_i}
\] (4a)
\[
= -\lambda - \tilde{\chi}_i,
\] (4b)

where, by summation over all atoms (from 1 to $N$), $\lambda$ can easily be found as the average electronegativity $\lambda = \frac{1}{N} \sum_{j=1}^N \tilde{\chi}_j$. The final equation for the fictitious charge motion is
\[
m_q\ddot{q}_i = \tilde{\chi} - \tilde{\chi}_i = \sum_{j=1}^N \frac{\tilde{\chi}_j - \tilde{\chi}_i}{N}.
\] (5)

For the equilibrated system $\ddot{q}_i \approx 0$, the following equation holds for the chemical potential by applying equation (1a),
\[
\mu = -\chi_i = -\tilde{\chi} \ \forall \ i \in [1, N].
\] (6)

Due to the different time scales of the nucleus and electron dynamics, the equations of motion for the nuclei and charges may be solved sequentially. This means that the nuclei may be interpreted as frozen background for the fictitious charge dynamics and only move
when the charges are equilibrated. A more detailed derivation and discussion of parameters can be found elsewhere [16].

In case of an external electric field \( \mathbf{E} = -\nabla \Phi \), the equation for the fictitious charge motion becomes

\[
m_q \ddot{q}_i = \ddot{X} - \ddot{\tilde{\chi}}_i = \sum_{j=1}^{N} \frac{\ddot{X}_j - \ddot{\tilde{\chi}}_i + \Phi_j - \Phi_i}{N},
\]

where \( \Phi_i \) and \( \Phi_j \) are the external electrostatic potential at the \( i \)-th and \( j \)-th atom site, respectively [24]. In line with the global charge transfer in EEM, QEq and ES+ (system is approximated as ideal conductor/metal), the polarization due to an external electric field is inherently the polarization of an ideal conductor (metal).

B. Extended Lagrangian method for QTPIE

While the charge transfer in EEM, QEq, and ES+ is inherently global (ideal conductor, metal), the charge transfer in QTPIE is inherently local (ideal insulator) [14]. This is achieved by the substitution of the neutral electronegativities \( \tilde{\chi}_i^0 \) with the effective electronegativities

\[
\tilde{\chi}_{eff,i}^0 = \sum_{j=1}^{N} c_{ij} \frac{\tilde{\chi}_i^0 - \tilde{\chi}_j^0}{N} S_{ij},
\]

where \( c_{ij} \) is a charge independent constant factor and \( S_{ij} \) is the \( ns \)-type overlap integral. In line with QEq, QTPIE makes use of \( ns \) Slater orbitals. Two suggestions for \( c_{ij} \) were made to maintain the correct scale of the atomic electronegativities,

\[
c_{1,ij} = \frac{N}{S_{ij}(r_0)}, \quad (9a)
\]
\[
c_{2,ij} = c_{2,i} = \frac{N}{\sum_{k=1}^{N} S_{ik}}. \quad (9b)
\]

A derivation is roughly outlined in the introduction and comprehensively described elsewhere [14 22 23].

To interpret QTPIE in the frame of an extended Lagrangian method, we apply equation (1b) to equation (4b) and substitute the electronegativities

\[
m_q \ddot{q}_i = -\lambda - \tilde{\chi}_{eff,i}^0 - \sum_{j=1}^{N} J_{ij} q_j
\]
\[
= -\lambda - \sum_{j=1}^{N} c_{ij} \frac{\tilde{\chi}_i^0 - \tilde{\chi}_j^0}{N} S_{ij} - \sum_{j=1}^{N} J_{ij} q_j,
\]
where the Lagrange multiplier $\lambda$ is determined by enforcing the charge neutrality constraint

$$
\lambda = -\frac{1}{N} \sum_{i=1}^{N} \left( \sum_{j=1}^{N} c_{ij} \frac{\tilde{\chi}_i^0 - \tilde{\chi}_j^0}{N} S_{ij} + \sum_{j=1}^{N} J_{ij} q_j \right). \quad (11)
$$

The resultant equation applying equation (11) to equation (10b), is, however, everything but intuitive to interpret. This can be attributed to the combination of local and global charge transfer, as well as their joint charge neutrality constraint.

For $c_{ij} = c_{2,ij}$, equation (11) cannot be further simplified due to the asymmetry of $c_{ij}$ ($c_{2,i} \neq c_{2,j}$). Global and local charge transfer interfere with each other while satisfying the charge neutrality constraint.

In case of $c_{ij} = c_{1,ij}$, the complexity of equation (11) can indeed be further reduced due to the symmetry of the overlap integral ($S_{ij} = S_{ji}$ and $c_{ij} = c_{1,ij} = c_{1,ji}$), thus

$$
\lambda = -\frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} J_{ij} q_j. \quad (12)
$$

As a result, local and global charge transfer satisfy the charge neutrality constraint individually, without interfering with each other.

For an external electric field $E = -\nabla \Phi$, the equation for the fictitious charge motion can be obtained by the appropriate substitution ($\tilde{\chi}_i^0 \rightarrow \tilde{\chi}_i^0 + \Phi_i$ and $\tilde{\chi}_j^0 \rightarrow \tilde{\chi}_j^0 + \Phi_j$).

While QTPIE is meant to approximate all systems as insulators, the combination of local and global charge transfer makes this or any other interpretation less straightforward. It is worthwhile to mention, however, that, similar to QEq, QTPIE may nonetheless be a powerful method.

Yet, it is not possible to simply constrain the global charge transfer in case of QTPIE. A reduced charge transfer due to the electrostatic interaction $J_{ij}$, would require a reduced electrostatic interaction $J_{ij}$ itself to maintain the model’s consistency.

III. PROPOSAL OF VARIABLE CHARGE MODELS

In the following, two models are presented which address the issue of global charge transfer inherent in many variable charge models. First, the charge transfer equilibration (QTE) model is described. The model is inspired by a comparison of the extended Lagrangian method applied to QEq (EEM, ES+) and QTPIE, adopting useful concepts. Second, an
extension to EEM, QEq and ES+ is discussed, which in a methodologically different way enables a better charge transfer for certain surface processes (i.e., adsorption, desorption). This method is inspired by the idea of dividing the system into subsystems (e.g., molecules) and defining an individual chemical potential for each \cite{16}.

A. Charge transfer equilibration (QTE)

In comparison with the previously discussed models, the charge transfer equilibration (QTE) approach differs essentially in two simple, but important decisions.

1. Scaled charge transfer variables

In QTPIE and SQE, charge transfer variables $q_{ij}$ are defined by $q_i = \sum_{j=1}^{N} q_{ij}$, whereas in QTPIE an additional scaling function is introduced to the neutral electronegativities to avoid distant charge transfer \cite{14, 17, 18, 22, 23}. Here, we utilize such a scaling function $f_{ij}$ to directly scale the charge transfer variables $q_{ij}$ themselves (i.e., the fictitious charge transfer per unit time)

$$\dot{q}_i = \sum_{j=1}^{N} f_{ij}\dot{q}_{ij}. \tag{13}$$

This means that the charge transfer in a given time interval $\delta t$ between atoms $i$ and $j$ is eventually suppressed by $f_{ij}$. Since the probability of an electron transfer from one to another orbital can be roughly approximated by the square of the respective overlap integral, it makes sense to claim $f_{ij} = c_{ij}S_{ij}^m$, where $c_{ij}$ is a constant for the fictitious charge (transfer) motion and the exponent $m$ needs still to be specified \cite{25}. $m$ was not chosen simply to be 2, because one has to take the difference between the charge model and physical reality into account. Specifically, the mentioned probability describes the likelihood of a single electron transfer, while in most variable charge models, charge is approximated to be continuous (i.e., a floating number). We believe, that it is therefore not straightforward to determine $m$. As shown later, the exponent has to satisfy $m \geq 1$ to allow for a non-vanishing computation of the gradient. While different values for $m$ might be viable, for simplicity, $m$ is chosen to be equal to 1. This choice does not impose any constraint on the general methodology.

To obtain a model which may be applicable for various RMD potentials, we did not specify the respective orbital on purpose. We believe, that the orbital (e.g., $ns$ Slater type orbital
or a linear combination of Gaussian type orbitals) should be chosen consistent with the
particular RMD potential of interest. This will be more thoroughly discussed in section VI.

As pointed out at the end of section II A, due to the different time scales of nuclei and
electrons, the respective equations of motion are solved sequentially and not in parallel.
The geometry of nuclei can therefore be thought of as static (frozen) background for the
fictitious charge motion. As a consequence, \( f_{ij} \), which may depend on the interatomic
distances, is a constant for the fictitious charge motion.

The transformation from atomic to charge transfer variables can thus be described by

\[
q_i - q_i(t = 0) = \sum_{j=1}^{N} c_{ij} S_{ij} q_{ij} \tag{14a}
\]

\[
\dot{q}_i = \sum_{j=1}^{N} c_{ij} S_{ij} \dot{q}_{ij} \tag{14b}
\]

\[
\ddot{q}_i = \sum_{j=1}^{N} c_{ij} S_{ij} \ddot{q}_{ij}. \tag{14c}
\]

2. Extended Lagrangian method for QTE

The second major difference in comparison to EEM, QEq, ES+ and QTPIE relates to
the considered quantity. Specifically, we evolve the interatomic charge transfer instead of
the atomic charge distribution in time. While most other models enforce charge neutral-
ity, \( \sum_{i=1}^{N} q_i = 0 \), here it is charge conservation that is considered, \( \sum_{i=1}^{N} \sum_{j=1}^{N} c_{ij} S_{ij} \dot{q}_{ij} = \sum_{i=1}^{N} \dot{q}_i = 0 \). The initial net charge of the system will therefore be kept constant during the
simulation. Since the method of the Lagrange multiplier inherently leads to a global charge
transfer, \( c_{ij} \) is required to satisfy the charge conservation constraint. The corresponding
equation of motion is evaluated through

\[ m_q \ddot{q}_{ij} = -\frac{\partial U}{\partial q_{ij}} \tag{15a} \]

\[ = -\frac{\partial U}{\partial q_i} \frac{\partial q_i}{\partial q_{ij}} - \frac{\partial U}{\partial q_j} \frac{\partial q_j}{\partial q_{ij}} \tag{15b} \]

\[ = -\dot{\tilde{\chi}}_i \frac{\partial q_i}{\partial q_{ij}} + \dot{\tilde{\chi}}_j \frac{\partial q_j}{\partial q_{ji}} \tag{15c} \]

\[ = -\tilde{\chi}_i \sum_{k=1}^{N} c_{ik} S_{ik} \frac{\partial q_k}{\partial q_{ij}} + \tilde{\chi}_j \sum_{k=1}^{N} c_{jk} S_{jk} \frac{\partial q_k}{\partial q_{ji}} \tag{15d} \]

\[ = -\tilde{\chi}_i \sum_{k=1}^{N} c_{ik} S_{ik} \delta_{jk} + \tilde{\chi}_j \sum_{k=1}^{N} c_{jk} S_{jk} \delta_{ik} \tag{15e} \]

\[ = -c_{ij} S_{ij} \tilde{\chi}_i + c_{ji} S_{ji} \tilde{\chi}_j \tag{15f} \]

\[ = c_{ij} S_{ij} (\tilde{\chi}_j - \tilde{\chi}_i). \tag{15g} \]

For equation (15b) we make use of equation (1a) using \( \tilde{\chi}_k = \frac{\partial U}{\partial q_k} \) and the symmetry of the charge transfer variables \( q_{ij} = -q_{ji} \); for equation (15d) we apply equation (14a). For equation (15g) we utilize the symmetry of the overlap integral \( S_{ij} = S_{ji} \) and claim \( c_{ij} = c_{ji} \). The latter means that the fictitious charge force \( f_{q,ij} \), which is defined by the right hand side of equation (15g), satisfies Newton’s third law \( f_{q,ij} = -f_{q,ji} \).

A pleasant result is that the charge conservation does in fact not depend on \( c_{ij} \) and is apparently inherently fulfilled. This can be tested by the summation over \( i, j \in [1, N] \).

The next goal is to transform the charge transfer variables back to atomic charge variables, starting from equation (15g). To achieve this, the equation is multiplied with \( c_{ij} S_{ij} \) and subsequently, the summation over \( j \in [1, N] \) is performed

\[ \sum_{j=1}^{N} c_{ij} S_{ij} m_q \ddot{q}_{ij} = \sum_{j=1}^{N} c_{ij}^2 S_{ij}^2 (\tilde{\chi}_j - \tilde{\chi}_i). \tag{16} \]

We then make use of equation (14c), obtaining

\[ m_q \ddot{q}_i = \sum_{j=1}^{N} c_{ij}^2 S_{ij}^2 (\tilde{\chi}_j - \tilde{\chi}_i). \tag{17} \]

The last unknown, \( c_{ij} \), is required to fulfill three specifications: i) symmetry \( c_{ij} = c_{ji} \), ii) agreement with QEq in the limiting case of global charge transfer \( (S_{ij} = 1) \), iii) sustaining
the local charge transfer. While \( c_{ij} \) can be defined in multiple ways, we propose here the following heuristic form

\[
c_{ij} = \frac{2}{\sum_{k=1}^{N} S_{ik} + S_{jk}}.
\]

(18)

The final equations of motion for atomic charge are then as follows

\[
m_{q} \ddot{q}_i = \sum_{j=1}^{N} \frac{4 S^2_{ij} (\tilde{\chi}_j - \tilde{\chi}_i)}{\left(\sum_{k=1}^{N} S_{ik} + S_{jk}\right)^2}.
\]

(19)

The electronegativity difference can be interpreted as upper limit for the instantaneous fictitious charge force. The quotient \( \frac{4 S^2_{ij}}{\left(\sum_{k=1}^{N} S_{ik} + S_{jk}\right)^2} \) functions as a weight for the latter. The overlap integral is put in relation to the sum of all neighboring overlap integrals, yielding the respective fraction. In total, the interatomic charge transfer is constrained by the orbital overlap distribution, resembling a network for the fictitious current.

With an external electric field \( \mathbf{E} = -\nabla \Phi \), the fictitious charge equations of motion become

\[
m_{q} \ddot{q}_i = \sum_{j=1}^{N} \frac{4 S^2_{ij} (\tilde{\chi}_j - \tilde{\chi}_i + \Phi_j - \Phi_i)}{\left(\sum_{k=1}^{N} S_{ik} + S_{jk}\right)^2},
\]

(20)

where \( \Phi_i \) and \( \Phi_j \) are the electrostatic potential at the \( i \)-th and \( j \)-th atom site, respectively.

For the \( i \)-th nuclei, the equations of motion are

\[
m_{i} \ddot{r}_i = -\nabla_i U - \sum_{j=1}^{N} \frac{\partial U}{\partial q_j} \nabla_i q_j
\]

(21a)

\[
= -\nabla_i U - \sum_{j=1}^{N} \frac{\partial U}{\partial q_j} \sum_{k=1}^{N} q_{jk} \nabla_i f_{jk}
\]

(21b)

\[
= -\nabla_i U - \sum_{j=1}^{N} \frac{\partial U}{\partial q_j} \sum_{k=1}^{N} q_{jk} (\delta_{ij} \nabla_i f_{ik} + \delta_{ik} \nabla_i f_{ji})
\]

(21c)

\[
= -\nabla_i U - \frac{\partial U}{\partial q_i} \sum_{k=1}^{N} q_{ik} \nabla_i f_{ik} - \sum_{j=1}^{N} \frac{\partial U}{\partial q_j} q_{ji} \nabla_i f_{ji}
\]

(21d)

\[
= -\nabla_i U - \tilde{\chi}_i \sum_{k=1}^{N} q_{ik} \nabla_i f_{ik} + \sum_{j=1}^{N} \tilde{\chi}_j q_{ij} \nabla_i f_{ij}
\]

(21e)

\[
= -\nabla_i U - \sum_{j=1}^{N} (\tilde{\chi}_i - \tilde{\chi}_j) q_{ij} \nabla_i f_{ij},
\]

(21f)

where the scaling function \( f_{ij} = c_{ij} S_{ij} \) may be used, in equation (21d) the symmetry of the charge transfer variables \( (q_{ij} = -q_{ji}) \), the overlap integral \( (S_{ij} = S_{ji}) \) and \( c_{ij} = c_{ji} \) is applied, and in equation (21e) equation (1a) \( (\tilde{\chi}_i = \frac{\partial U}{\partial q_i}) \) is used.

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The net charge transfer $q_{ij}$ for the current atom geometry can be obtained by integrating twice the time evolution described in equation (15g), where $c_{ij}$ is defined by equation (18),

$$\int \int \dot{q}_{ij} dt^2 = q_{ij} + q_{ij}(t = 0) + \dot{q}_{ij}(t = 0)$$  \hspace{1cm} (22a)

$$= \frac{1}{m_q} \int \int \frac{2S_{ij}(\tilde{\chi}_j - \tilde{\chi}_i)}{\sum_{k=1}^{N} S_{ik} + S_{jk}} dt^2,$$  \hspace{1cm} (22b)

where $q_{ij}(t = 0)$ and $\dot{q}_{ij}(t = 0)$ stem from the preceding charge equilibration run (former atom geometry) and initially are set to 0.

The $i$-th gradient of the scaling function $f_{ij} = c_{ij}S_{ij}$ is described by

$$\nabla_i f_{ij} = \frac{2}{\sum_{k=1}^{N} S_{ik} + S_{jk}} \left( \nabla_i S_{ij} - \frac{S_{ij} \nabla_i S_{ij} + S_{ij} \sum_{l=1}^{N} \nabla_i S_{il}}{\sum_{k=1}^{N} S_{ik} + S_{jk}} \right),$$  \hspace{1cm} (23)

A thorough discussion on parameters and how to set up the extended Lagrangian method (e.g., convergence criteria) can be found elsewhere [16].

To generalize this model without applying the extended Lagrangian method (e.g., in the frame of ReaxFF), the $i$-th of the system of $N$ linear equations can be obtained by setting $\ddot{q}_i$ to zero in equation (20),

$$\sum_{j=1}^{N} 4S_{ij}^2 (\tilde{\chi}_j - \tilde{\chi}_i + \Phi_j - \Phi_i) \left( \sum_{k=1}^{N} S_{ik} + S_{jk} \right)^2 = 0.$$  \hspace{1cm} (24)

One may use $\tilde{\chi}_i = \tilde{\chi}_i^0 + \sum_{j=1}^{N} q_{ij}J_{ij}$ (i.e., equation 1b) to determine the electronegativity. If no external electric field is applied, $\Phi_i$ and $\Phi_j$ have to be set to zero.

Without the extended Lagrangian method the force $\mathbf{F}_i$, which acts on the $i$-th atom, is described by the right hand side of equation (21f). The time integral for the computation of $q_{ij}$ in equation (22b) may be evaluated as the sum of the respective iterations during a single charge equilibration run.

**B. Extension to EEM, QEq and ES+ for specific surface processes**

QTE is proposed to inherently account for varying charge transfer conditions encountered in numerous surfaces processes (e.g., dissociation, recombination, desorption, adsorption, sputtering, deposition, fragmentation). In the following, in contrast, an alternative to the preceding model is described, which enables EEM, QEq and ES+ to treat a few surface
processes (i.e., adsorption, desorption) appropriately, too. In the introduction an approach was mentioned, where the system is divided into subsystems (e.g., molecules) and multiple chemical potentials (one per subsystem) are defined \[16\]. Here, we simply divide our system into \( N + 1 \) subsystems. The first one is the surface with the chemical potential \( \mu \). The other ones are a replicate of the former, where each atom’s charge is set individually to zero, defining \( \mu_{0,i} \) chemical potentials. An atom at a distance from the surface slab is therefore enforced to be neutral. At last, a tapering function \( f_i(r_i) \) (e.g., the Tersoff cutoff function used in COMB3 or the tapering function used in ReaxFF \[10, 12\]) is utilized to create a smooth transition from the first to the second chemical potential. The transition region may be defined by the lower and upper bound \( h_{lo} \) and \( h_{hi} \), respectively, along the surface normal \( \mathbf{n} \). The tapering function must satisfy \( f_i(r_i) = 1 \) for \( r_i \leq h_{lo} \) and \( f_i(r_i) = 0 \) for \( r_i \geq h_{hi} \). We suggest to choose \( h_{lo} \) slightly above the last atom in \( \mathbf{n} \) direction. If the potential of interest (e.g., ReaxFF, COMB3) employs a cutoff radius \( r_c \), \( h_{hi} \) can be simply chosen to be \( h_{hi} = r_c \).

For deposition or sputtering simulation, however, it may be a good practice to regularly adjust both bounds, due to the variation of the surface height in \( \mathbf{n} \) direction. Using equation (6), the \( i \)-th linear equation for the atomic charge distribution becomes

\[
\begin{align*}
&f_i \mu + (1 - f_i) \mu_{0,i} = 0 \quad (25a) \\
\iff &f_i \left( \sum_{j=1}^{N} \frac{\tilde{X}_j - \tilde{X}_i}{N} \right) + (1 - f_i) \left( \sum_{j=1}^{N} \frac{\tilde{X}_j|q_i=0 - \tilde{X}_i|q_i=0}{N} \right) = 0. \quad (25b)
\end{align*}
\]

IV. MIRROR BOUNDARY CONDITION

Surface simulations typically employ a slab, which often is created by cleaving the respective bulk system perpendicular to the surface normal \( \mathbf{n} \). This slab is often meant to be an approximation for the surface and bulk system of interest, taking the second (lower) surface as necessary circumstance. Thus, the interaction between both surfaces is in many cases highly undesirable. This issue is typically addressed by creating a thicker slab to suppress the respective interaction. The increased thickness, however, consequently enlarges the computational cost. Furthermore, the atoms which belong to the lower surface are usually not evolved in time (frozen), avoiding unnecessary computations and fixing the slab position. In case of RMD simulations, specifically variable charge models, the lower surface imposes nonetheless additional computational effort. While the nuclei at the lower surface can be
kept frozen, the charge, however, has to be equilibrated throughout the total system. This circumstance is substantial, if one considers that charge equilibration is usually one the most time consuming aspects of RMD simulations.

In the following, a mirror boundary condition (MBC) is described which overcomes this computational burden. A symmetry for the lower bound of the simulation box in \( \mathbf{n} \) direction is introduced, which enforces all atoms beneath the specified height \( h_{hi} \) to interact with each other as well as with their mirror images. Mirror images are replicates of the original atoms with inverted \( \mathbf{r} \cdot \mathbf{n} \) coordinate. The respective domain will be referred to as mirroring zone.

For RMD potentials that make use of a cutoff radius \( r_c \) (e.g., ReaxFF, COMB3), \( h_{hi} \) should be chosen to be slightly larger than \( r_c \). It is recommended to exclude the nuclei below \( h_{hi} \) from the time integration (frozen) to avoid introducing artifacts into the dynamics. Overall, the MBC corresponds to a homogeneous Neumann boundary condition for the total potential energy \( U \),

\[
\frac{\partial U}{\partial \mathbf{n}} = 0. 
\]  

There are many crystal structures, however, that do not allow for this kind of introduced symmetry. To enlarge the number of possible materials, a lower bound \( h_{lo} \) for the mirroring zone is defined. The latter should be chosen to only include the first layer of atoms, which should be positioned very close the lower bound of the simulation box in \( \mathbf{n} \) direction. Then, the atoms in this first layer do not have any mirror images (while interacting with the other atoms and their mirror images). Though, this first layer of atoms has to be charge neutral to sustain charge conservation (or charge neutrality) of the total system. Unfortunately, this reduces the number of potential crystals structures to be studied. The MBC is nonetheless beneficial for the remaining ones (e.g., rocksalt lattice structure). A schematic of the MBC for B1 TiN (rocksalt lattice structure) is presented in figure[1].

Whenever a global quantity (e.g., net charge, total energy, stress tensor) is computed as a function of all atom properties, care has to be taken to account for the mirror images appropriately. For example, when checking for charge neutrality (or charge conservation), the net charge \( Q \) of the system is described by

\[
Q = \sum_{i=1}^{N} q_i (1 + (r_i \cdot \mathbf{n} > h_{lo})) 
\]  

It is worthwhile to mention that, while the MBC can be very useful to study a variety of
Figure 1. Schematic representation of the mirror boundary condition for B1 TiN (rocksalt lattice structure). Titanium and nitrogen atoms are coloured grey and blue, respectively. The depicted slab width, thickness, $h_{hi}$ and $h_{lo}$ are meant to illustrate the concept and do not correspond to appropriate choices for a RMD simulation. From top to bottom: atoms, frozen atoms, frozen atoms without mirror images, mirror images of frozen atoms, mirror images of atoms.

surface processes, it may not be used to evaluate thermodynamic quantities.

V. IMPLEMENTATION

The implementation of the preceding models is often straightforward. In the following, however, we are going to highlight a few advisable aspects. All models are implemented in the widely used open-source code LAMMPS \[21\].

First, a few basics concerning the parallelization in LAMMPS are provided. Each processor handles a subdomain of the total simulation box. Ghost atoms are used to allow for atoms to interact with each other while being owned by different processors. This is in particular useful for boundary conditions. Each atom keeps all its ghost atoms up to date (e.g., concerning atom site and charge). The ghost atoms, on the other hand, transfer the experienced force (and fictitious charge force) back to the real atoms. The migration from one to another processor can be triggered if an atom leaves the respective subdomain. The migration,
however, will only be executed, when the neighborlist is built the next time.

The implementation of the extended Lagrangian method in combination with a Verlet algorithm may cause harm, when an atom migrates from one to another processor. The latter may have no information about the fictitious charge force of the atom, which consequently leads to a violation of the charge conservation (and charge neutrality). Yet, this issue can straightforwardly be dealt with: When the neighborlist is rebuilt during the nuclei timestep, the subsequent fictitious charge motion are restarted ($\tilde{q}_i = \dot{q}_i = 0 \ \forall \ i \in [1, N]$) from the current atomic charge distribution $q_i$. Even when its unnecessary (no atom migration between processors), this procedure does no harm to the respective fictitious charge dynamics.

For the implementation of QTE (and QTPIE), the overlap integrals have to be evaluated only once for each charge equilibration run (nuclei are frozen).

The implementation of the MBC can be easily achieved utilizing the ghost atom concept in LAMMPS. When setting up the simulation, each atom with $r \cdot \mathbf{n} \in [h_{lo}, h_{hi}]$ is used to create its own mirror image as ghost atom (the respective processors are marked with a mirror flag). Naturally, the atoms will then update their mirror images. Subsequently, the processors share the ghost atoms with each other. Thus, the interactions between atoms and mirror images will be performed self-consistently.

When Newton’s 3rd law is used to reduce the number of computations, the implementation of the MBC becomes more complicated. In LAMMPS, the application of Newton’s 3rd law leads to the iteration over the atom tags $i > j$ instead of all $i, j \in [1, N]$. Tags are used for this purpose instead of indices. The atom with the tag $j$ corresponds to a neighbor of the atom with the tag $i$. The neighborlist of the atom with the tag $i$ never includes itself, so that it would be safe to iterate over $i \geq j$. While this is typically redundant, in the presence of the MBC the atom with the tag $i$ may have a mirror image whose tag is copied from the real atom $i$. We therefore iterate over $i \geq j$ instead of $i > j$. Furthermore, three exceptions at the MBC have to be considered specifically. As mentioned in section IV, nuclei are meant to be excluded from the time integration (frozen). Thus, only the scalar fictitious charge forces $f_{q,ij}$ have to be adapted. They are defined by

$$m_q \ddot{q}_i = \sum_{j}^{N} f_{q,ij} \tag{28}$$

and can be determined in comparison with equations (5), (10b) and (19) for EEM (QEq, ES+), QTPIE and QTE, respectively. The fictitious charge forces at the MBC have to be
adapted as follows

\[ f_{q,ji} \rightarrow 0 \quad \text{if} \quad (h_{lo} < r_i \cdot n < h_{hi}) \quad \text{and} \quad i = j \quad \text{(self mirror image)} \quad (29a) \]

\[ f_{q,ji} \rightarrow 2f_{q,ji} \quad \text{if} \quad (h_{lo} < r_i \cdot n < h_{hi}) \quad \text{and} \quad (|r_j \cdot n| < h_{lo}) \quad (29b) \]

\[ f_{q,ji} \rightarrow 0 \quad \text{if} \quad (|r_i \cdot n| < h_{lo}) \quad \text{and} \quad (h_{lo} < -r_j \cdot n < h_{hi}), \quad (29c) \]

where the last two adaptations equations (29b) and (29c) are only necessary when \( h_{lo} \) differs from the lower bound of the simulation domain in the surface normal direction \( n \). As mentioned in section IV, the net charge of the atoms which satisfy \((|r_i \cdot n| < h_{lo})\) has to equal zero to avoid a violation of the charge conservation (and charge neutrality).

VI. CONCLUSION

The charge transfer equilibration (QTE) model described in section III.A is a generalization of QEq (or EEM, ES+) and corresponds to the latter for a hypothetical global charge transfer, \( S_{ij} = 1 \). QEq, EEM and ES+ are based on a global charge transfer, approximating each system as an ideal conductor (metal). QTPIE is meant to approximate each system as ideal insulator. In QTE, the range and intensity of the charge transfer is self-consistent. The orbital overlap distribution of the respective atom geometry can be thought of corresponding to a network for the interatomic charge transfer.

Consequently, the same holds for the polarization of the system due to an externally applied electric field. Still, the former enables polarization only along bonds. This is a limitation for any atomic charge model. For a more sophisticated polarization model, dipoles as additional degree of freedom have to be introduced [12, 26].

While the orbital of the valence electrons can be described by a variety of orbital types, we believe that the latter should be chosen consistent with the outer RMD potential model. For example, if one would like to replace QEq with QTE, an \( ns \) Slater type orbital (STO) may be used. In combination with COMB3, where a \( Z+1s \) STO is used for the electrostatic interactions (ES+), a 1s STO should be used to for the QTE model. (\( Z \) is the charge of the nuclei.) For the old version of ReaxFF, where EEM is applied and thus, no orbitals are made use of, a linear combination of three Gaussian type orbitals (STO-3G) could be considered. In the current version of ReaxFF, ACKS2 is made use of. The orbital exponent for the QTE model can either be taken from the outer potential model or be fitted to the
respective overlap integrals.

While the evaluations of the latter cause additional computational cost, our experience indicates that the QTE model is even faster than QEq (in combination with COMB3, a factor of approximately 2 is achieved). This can be reasoned in the locality, which eventually requires less iterations until the atomic charge distribution is converged.

All in all, QTE may serve as an alternative to ACKS2, which is based on a differing approach. When choosing between ACKS2 and QTE, one has to weigh individually, which model suits the respective simulation framework, RMD potential and application best.

The extension to EEM, QEq and ES+, described in [1], deals effectively with the global charge transfer in certain surface processes (e.g., adsorption and desorption). The evaluation of $\tilde{\chi}_i|q_i=0$ and $\tilde{\chi}_j|q_i=0$ in equation (25b), however, increases the computational cost slightly. Though, the greatest disadvantage is that the charge transfer between for example sputtered particles is weakened and eventually omitted. Moreover, the scaling of the charge transfer by a tapering function appears to us less sophisticated than the application of an overlap integral. Though, this model may find its applicability in certain cases.

The mirror boundary condition (MBC), described in section IV, speeds up RMD surface simulations that employ variable charge models. Our experience with the MBC indicates that RMD (i.e., COMB3) simulations of thin ($\approx 30$ Å) surface slabs can be sped up by a factor of approximately 2. Though, as pointed out in section V, there are a few exceptions that have to be considered when implementing the MBC.

A sufficient presentation and discussion of the mentioned preliminary studies (i.e., of metal nitrides) goes beyond the scope of this paper and will be subject to future publications.

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