

Merging bond-order potentials with charge equilibration

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A method is presented for extending any bond-order potential (BOP) to include charge transfer between atoms through a modification of the split-charge equilibration (SQE) formalism. Variable limits on the maximum allowed charge transfer between atomic pairs are defined by mapping bond order to an amount of shared charge in each bond. Charge transfer is interpreted as an asymmetry in how the shared charge is distributed between the atoms of the bond. Charge equilibration (QE) assesses the asymmetry of the shared charge, while the BOP converts this asymmetry to the actual amount of charge transferred. When applied to large molecules, this BOP/SQE method does not exhibit the unrealistic growth of charges that is often associated with QE models. [doi:10.1063/1.3271798]

The concept of bond order as a characterization of the strength of covalent bonds has been used extensively to develop empirical potentials suitable for molecular dynamics (MD) simulations.^{1–7} Part of the attraction of a continuous variable bond order is it allows for a natural interpolation between bonded and nonbonded states, making it suitable for modeling reactive systems. The reactive empirical bond order (REBO) potential developed by Brenner,^{2,3} which itself is based on the formalism of Tersoff,¹ is an example of such a potential; and, in fact, several bond-order potentials (BOPs) adopt Brenner's formalism.^{4,6,7}

In systems containing atoms with significantly different electronegativities, charge transfer and the electrostatic interactions between the resulting charged atoms are of critical importance. Charge-equilibration (QE) methods based on electronegativity equalization have been applied to relatively homogeneous small-molecule systems near equilibrium,^{8–10} but tend to give charges and molecular dipole moments that are too large when applied to large molecules.^{11–14} Three general approaches to dealing with this problem are (1) optimization of model parameters for the particular systems under investigation,^{15,16} (2) constraining of subentities of large molecules to be charge neutral,^{14,17} and (3) reformulation of QE in the language of charge transfer between pairs of atoms along with the addition of controls over how pairs are allowed to exchange charge.^{12,18–23} The formalism of BOPs is one centered on atomic pairwise interactions modified by the surrounding chemical environment; consequently, approach (3) is a natural one for integration with BOPs. The key idea is to use a map that connects the continuous valued bond order to a shared charge in a covalent bond. Charge transfer is interpreted as the shared charge being more concentrated with one atom versus the other. This simple and novel idea brings bond-strength considerations into the QE process allowing, for instance, double bonds to more freely transfer charge than single bonds.

In a bond-centered approach, the charge Q_i of atom i is the sum of all charges transferred to it across each of its bonds ("split charges," as they are referred to by Nistor *et al.*²¹), \bar{q}_{ij} ,

$$Q_i = \sum_j \bar{q}_{ij}. \quad (1)$$

The index j runs over the set of atoms to which atom i is bonded and \bar{q}_{ij} is the charge transferred to atom i from atom j . By the constraint $\bar{q}_{ij} = -\bar{q}_{ji}$, split-charge equilibration (SQE) methods take each split-charge pair as a neutral entity to be equilibrated.

In the case of an isolated diatomic molecule composed of atoms i and j , equilibrium is characterized by the minimization of a charge potential of the form

$$\bar{V} = -|\chi_i - \chi_j| \bar{q} + \frac{1}{2} J_{ii}^0 \bar{q}^2 + \frac{1}{2} J_{jj}^0 \bar{q}^2 - J_{ij} \bar{q}^2. \quad (2)$$

Here, χ_i and χ_j are atomic electronegativities with atom j taken to be more electronegative; \bar{q} is the split-charge magnitude, $\bar{q} = \bar{q}_{ij} = -\bar{q}_{ji}$; J_{ij} is the Coulomb interaction-energy of unit-charge distributions centered on the locations of atoms i and j ; J_{ii}^0 and J_{jj}^0 are $r=0$ limiting cases where the factors of 1/2 address the double counting that occurs in a self-energy as opposed to interaction calculation. The screened Coulomb interactions associated with overlapping charge distributions are often calculated with the use of either Slater orbitals^{8,9,18} or Gaussian orbitals.^{24,25} Independent of how the shapes of charge distributions are approximated, the self-energy terms will dominate over the interaction term; thus, the \bar{q}^2 terms above, taken together, imply a restoring charge force that balances the constant drive to transfer charge associated with the difference in electronegativity between the atoms. Differentiating with respect to \bar{q} and converting back to the language of the split-charges \bar{q}_{ij} and \bar{q}_{ji} , the equilibrium condition becomes

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$$\chi_i + J_{ii}^0 \bar{q}_{ij} + J_{ij} \bar{q}_{ji} = \chi_j + J_{jj}^0 \bar{q}_{ji} + J_{ij} \bar{q}_{ij}. \quad (3)$$

Each side can be thought of as a charge-dependent electronegativity for one side of the bond.

For a bond in an electrostatic environment, the basic idea is the same: Each bond is a neutral entity that settles into an internal equilibrium. When equilibrating a split-charge pair, all other split charges are simply charges that contribute to the electrostatic environment. Gathering split charges whenever possible to assemble atomic charges, the charge-dependent electronegativity associated with \bar{q}_{ij} takes the form

$$\bar{\chi}_{ij} = \chi_i + J_{ii}^0 Q_i + \sum_{k \neq i} J_{ik} Q_k. \quad (4)$$

This electronegativity for the i side of bond ij depends only on total atomic charges with no special reference to the j side of the bond. This implies that all bonds connected in a network will equilibrate to the same charge-dependent electronegativity. Interestingly, this SQE model yields the same charge assignments as the analogous QE model that uses the same atomic electronegativities and unit-charge Coulomb interactions. In fact, it has been shown that even in a more general SQE approach, where fixed atomic electronegativities are replaced with pairwise geometry-dependent electronegativities, there exists an equivalent formulation in terms of atomic-charge variables.¹⁹

A reformulation in atom space rather than bond space can reduce the computational cost of determining atomic charges via matrix methods; however, carrying out SQE in bond space need not impose a computational cost over a QE approach if integration with the BOP is carried out thoughtfully. Two aspects are worth taking note of: (1) An extended Lagrangian approach rather than matrix methods can be used to evolve charges in a manner that mirrors the MD evolution of atomic positions.⁹ The extended Lagrangian approach does not suffer the scaling problems associated with matrix methods. Furthermore, with a proper choice of the fictitious charge mass, charge updates can be carried out with the same frequency as atomic position updates. This one-for-one approach will yield approximate charges for each instantaneous geometric configuration that are suitable in the context of MD. If more accurate results are desired, several charge-update iterations can be carried out for each atomic position update.²⁶ (2) If only nonzero bond-order pairs are allowed to transfer charge, the number of split-charge pairs will scale linearly with the number of atoms; furthermore, the generation and maintenance of the list of such pairs is handled by the BOP, and so poses no further computational cost.

With the SQE approach outlined above giving the same result as its analogous QE approach, the problem of overestimation of dipole moments of large molecules is not solved merely by adopting the SQE formalism. An approach is needed whereby each bond partly decouples from its bond network and settles into its own equilibrium $\bar{\chi}$. Fortunately, there is a simple modification that accomplishes this in a physically motivated way in the context of BOPs. The essential idea is to connect the bond order of each bond to an amount of shared charge in each bond and to interpret split

charge as an imbalance in where the shared charge is concentrated. Split charges cannot grow in size beyond this shared-charge limit, and if the nature of the bond is covalent, the size of the split charges should not even get close to this limit. Defining the fractional split charge \bar{f}_{ij} as the ratio of the split charge on atom i transferred from atom j to its shared charge \bar{q}_{ij}^{\max} , the charge on atom i is expressed as

$$Q_i = \sum_j \bar{f}_{ij} \bar{q}_{ij}^{\max}. \quad (5)$$

The shared-charge limit is calculated directly from the bond order b_{ij} assigned to the bond from the BOP, $\bar{q}_{ij}^{\max} = \bar{q}_{ij}^{\max}(b_{ij})$. Focus is shifted from equilibrating split charges to equilibrating fractional split charges. The equilibration process assesses how asymmetric the sharing of charge is; the BOP fixes how much charge is actually shared (a quantity that in reactive systems smoothly goes to zero as a bond dissolves until fully broken).

Driving the equilibration process for bond ij will be three elements: (1) The constant pull to increase charge separation associated with the traditional constant electronegativity difference $|\chi_i - \chi_j|$; (2) Coulomb interactions within the bond and with the surrounding environment; (3) a restoring force that approaches an infinite wall as the shared-charge limit is approached. The first two elements carry over without change from the discussion above, the only difference being that the equalization condition is interpreted as applying to \bar{f}_{ij} rather than \bar{q}_{ij} . The third element can be implemented through an inverse hyperbolic tangent function added to the charge-dependent electronegativity of each fractional split charge,

$$\bar{\chi}_{ij} = \left[\chi_i + J_{ii}^0 Q_i + \sum_{k \neq i} J_{ik} Q_k \right] + \bar{\epsilon}_{ij} \tanh^{-1}(\bar{f}_{ij}). \quad (6)$$

The notation $\bar{\chi}_{ij}$ refers to the variable electronegativity of atom i in the context of bond ij . The scale parameter $\bar{\epsilon}_{ij}$ can, in general, be tailored to each pair of atom types. With large $\bar{\epsilon}_{ij}$ values, the wall gradually rises as soon as split charges grow; very small values limit the influence of the wall while charges are small although the approach to infinity kicks in sharply as the shared-charge limit is neared. For ease of implementation, $\tanh^{-1}(x) = \frac{1}{2} \ln[(1+x)/(1-x)]$ in the range of concern, $-1 < x < 1$.

The charge-asymmetry penalty term $\bar{\epsilon}_{ij} \tanh^{-1}(\bar{f}_{ij})$ serves not only to physically constrain the growth of split charges but also partly decouples each bond from its bond network; SQE becomes a locally driven process that does not map back to the global equilibration of an entire molecule. It is also the case that there are statistical mechanical arguments that can be connected with the QE formalism that suggest the use of an inverse hyperbolic tangent function.²⁷⁻³⁰ Nonetheless, alternate choices which possess the required asymptotic behavior could be explored. For instance, once $\bar{\epsilon}_{ij}$ parameters are fitted, a tangent function yields nearly the same form as the inverse hyperbolic tangent for $|\bar{f}_{ij}| \lesssim 0.4$; outside this range, the wall rises more quickly with the tangent function,

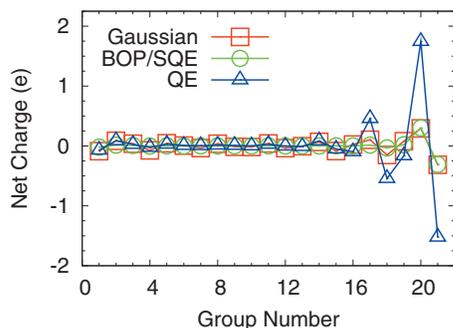


FIG. 1. Group charges for the alcohol $\text{CH}_3(\text{CH}_2)_{19}\text{OH}$ where the CH_3 group takes group No. 1 and the OH group takes group No. 21. Shown are a DFT calculation performed with Gaussian (B3LYP 6-31G*, CHELPG charges) and results from the preliminary BOP/SQE model and its closest analogy QE model.

and thus this choice would exhibit less charge transfer in extreme environments such as molecules in the presence of strong electric fields.

It remains to specify how to map bond order b_{ij} to shared charge $\bar{q}_{ij}^{\text{max}}$. How this is done can be tailored to each pair of atom types. In BOPs where a strong double bond is assigned a bond order that is roughly twice that of a strong single bond, a simple linear map is sufficient,

$$\bar{q}_{ij}^{\text{max}}(b_{ij}) = b_{ij}/b_{ij}^{\text{ref}}. \quad (7)$$

The parameter b_{ij}^{ref} can be fixed by requiring that a strong single bond with the atom types of atoms i and j in a chosen reference molecule maps to one shared electron.

At this stage, it is perhaps best to use a simple approach so as to not unintentionally suggest that problems are being addressed merely by introducing a host of new parameterizing possibilities. To that end, single values for $\bar{\epsilon}$ and b^{ref} can be applied to all types of atomic pairs, and parameters that map back to QE methods can be taken directly from Rappé and Goddard.⁸ The required QE parameters are χ and ζ for carbon, hydrogen, and oxygen; the ζ parameters fix the shapes of the Slater orbitals used to calculate $J_{ij}(r_{ij})$.

In Rappé and Goddard's original QE method, hydrogen is treated specially with a charge-dependent $\zeta_{\text{H}}(Q_{\text{H}})$ that grows linearly with Q_{H} . It is common, however, to simply adopt constant values for all atom types.^{9,18} Without a charge-dependent ζ_{H} , Q_{H} will, in general, grow too large; typically this is dealt with by adopting a value for ζ_{H} that is larger than Rappé and Goddard's value at $Q_{\text{H}}=0$. Here, we tune $\bar{\epsilon}$ to water to give a dipole moment of 1.850 D for $r_{\text{OH}}=0.9578 \text{ \AA}$ and $r_{\text{HH}}=1.5144 \text{ \AA}$ while retaining the $\zeta_{\text{H}}(Q_{\text{H}}=0)$ value from Rappé and Goddard. This choice for $\bar{\epsilon}$ can be made independent of any particular BOP if b^{ref} is chosen to give a shared charge of one electron to each OH bond in this reference situation. This preliminary model results in $\bar{\epsilon}=3.340 \text{ eV}$. For comparison, a closest analogy QE model is adopted using the same Rappé and Goddard parameters with the exception of a constant ζ_{H} chosen to also give the experimental dipole moment for water. This requires $\zeta_{\text{H}}=1.5812 \text{ a.u.}^{-1}$ compared to $\zeta_{\text{H}}(Q_{\text{H}}=0)=1.0698 \text{ a.u.}^{-1}$ originally used by Rappé and Goddard.⁸

Figure 1 compares the charge assignments (net charges on the CH_3 , CH_2 , and OH groups) resulting from density

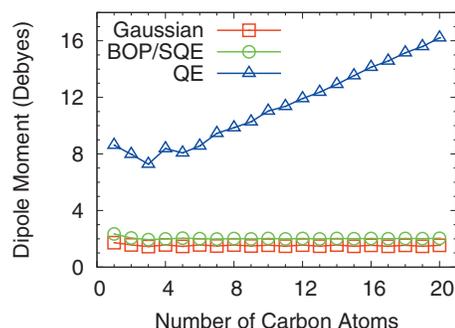


FIG. 2. Dipole moments of alcohols as a function of alcohol length (number of carbon atoms). Shown are a DFT calculation performed with Gaussian (B3LYP 6-31G*, CHELPG charges), and results from the preliminary BOP/SQE model, and its closest analogy QE model.

functional theory (DFT), the BOP/SQE model, and the closest analogy QE model for an alcohol containing 20 carbon atoms. In all cases, the geometry was held fixed. The DFT calculation was performed with Gaussian using B3LYP 6-31G*; charges from electrostatic potentials using a grid based method (CHELPG) (Ref. 31) charges are shown. With the CHELPG method, atomic charges are fitted to match the electrostatic potential over a grid of points surrounding a molecule. This method can be problematic when applied to large volume structures containing atoms far removed the structure's surface; in such cases, Mulliken charges may prove more useful. With alcohols, all atoms are close to the surrounding grid surface on which the electrostatic potential is fit, suggesting that CHELPG charge assignments for comparative purposes are useful in this case. The adaptive intermolecular reactive empirical bond-order (AIREBO) potential⁴ was used only to calculate bond orders for the BOP/SQE model. For the BOP/SQE and QE models, charges were calculated using an extended Lagrangian approach.⁹ The inability of QE methods to handle large molecules is clearly evident, and the similarity between the BOP/SQE and DFT results is very encouraging considering that no fitting has been done aside from tuning $\bar{\epsilon}$ to obtain the dipole moment of water.

Figure 2 shows the length dependence of the dipole moments of alcohols. The results from DFT and the BOP/SQE model show a remarkable similarity considering that most parameters of the BOP/SQE model are shared in common with the QE model. Both the DFT and the BOP/SQE results show an approximate 10% drop in dipole moment at long lengths compared to short lengths; the QE model shows the unrestrained growth that is a general problem with models of this type.

Here, the particular case of alcohols has been discussed; however, the BOP/SQE approach offers resolutions to a number of problems that arise in QE methods. Of foremost importance is the limiting of charge transfer at the bond level through the use of a bond order to shared-charge map. In addition, molecular distinctions are no longer required; each pair of atoms with nonzero bond order is a charge-neutral subsystem that is equilibrated. Molecules can be identified through an analysis of bond networks, although these identifications are not required. This is particularly important in

reactive systems where the identification of molecules becomes vague when bonds are in the process of breaking and forming. The inclusion of very weak bonds that get assigned fractional split charges is not problematic because appreciable charge transfer occurs only once the bond order grows large enough. In other words, the smooth interpolation between bonds that can and those that cannot exchange charge is handled by the BOP and has little to do with the equilibration process that sets the fractional split charges for each bond.

The above described method for creating a BOP/SQE hybrid method presents three practical advantages: (1) Ease with which the SQE can be integrated with any BOP; (2) assurance of nonpathological behavior due to its basic design; (3) the lack of any need to explicitly identify molecules or molecular subentities that are to be constrained as charge neutral and equilibrated. Consequently, this BOP/SQE method should prove very useful in modeling a variety of reactive dynamic systems.

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