EPJ manuscript No.
(will be inserted by the editor)

The chemical hardness of molecules and the band gap of solids within charge equilibration formalisms

Toward force field-based simulations of redox reactions

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Received: date / Revised version: date

Abstract. This work finds that different charge equilibration methods lead to qualitatively different responses of molecules and solids to an excess charge. The investigated approaches are the regular charge equilibration (QE), the atom-atom-charge transfer (AACT), and the split-charge equilibration (SQE) method. In QE, the hardness of molecules and the band gap of solids approaches zero at large particle numbers, affirming the claim that QE induces metallic behavior. AACT suffers from producing negative values of the hardness; moreover valence and conduction bands of solids cross. In contrast to these methods, SQE can reproduce the generic behavior of dielectric molecules or solids. Moreover, first quantitative results for the NaCl molecule are promising. The results derived in this work may have beneficial implications for the modeling of redox reactions. They reveal that by introducing formal oxidation states into force field-based simulations it will become possible to simulate redox reactions including non-equilibrium contact electrification, voltage-driven charging of galvanic cells, and the formation of zwitterionic molecules.

PACS. 34.70.+e Charge transfer – 77.22.-d Dielectric properties of solids and liquids – 34.20.Cf Interatomic potentials and forces

1 Introduction

In the quest for transferable force fields, it is necessary to construct models allowing one to predict meaningful partial charges of atoms and molecules so that long-range

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[a] The author greatfully acknowledges discussions with Wolf Dapp and Carlos Campana.

electrostatic interactions can be computed accurately [1, 2]. The general strategy to capture the electrostatics of molecules, clusters, and solids is to minimize an expression for the energy $V(\{Q\})$ with respect to the set of atomic charges $\{Q\}$ [3], and potentially also with respect to dipoles or higher-order multipoles [4]. Important terms in these approaches are related to the electronic chemical potential [5,6] and the chemical hardness [5,7] of atoms as well as the Coulomb interaction between the atoms [3]. Those terms can be motivated from the density functional theory (DFT) formulation of quantum mechanics [3,7,8], which is based on minimizing an energy functional that depends on continuous (charge) densities rather than an energy function of discrete charges and multipoles.

Many different approaches have been pursued to construct $V(\{Q\})$, the most prominent being the chemical potential equalization method [3], which is also known as charge equilibration (QE) approach [9]. Here, the relevant degrees of freedom are solely atomic charges. More recent approaches, such as the atom-atom charge transfer (AACT) model [10], are based on the idea that charges must be donated across a chemical bond. In the original AACT formulation, hardness was only associated with charge transfer through a chemical bond but not with the atomic charges themselves. The split-charge equilibration (SQE) method [11] overcame this limitation by combining the terms contained in AACT and QE. Although both QE and AACT formally arise as opposite limiting cases of SQE, realistic parameterizations [11,12] always found finite but relatively small bond hardnesses so that AACT should not arise as a limiting case of SQE in practice.

The quality of a charge equilibration formalism is usually evaluated by assessing to what extent the energy function can be motivated from first principles [13,14] or how well it can reproduce electrostatic potential surfaces, partial charges, or polarizabilities as computed in quantum chemical or DFT calculations [13,12]. Limited attention has been paid to the question of what *collective* properties the various schemes produce *generically* when applied to a large number of atoms. Establishing relationships between collective response functions and the coefficients used in a charge equilibration model can then aid in the validation or falsification of the analyzed model, or guide its further refinement. Moreover, parameter calibration, which sometimes turns out ill-defined when fitting to partial charges alone [15], can be facilitated by the knowledge of how response functions constrain the choice for the microscopic interaction parameters.

Regular, purely atom-based QE models have been shown to suffer from the following generic problems, which do not depend on the details of the parameter calibration: (i) They produce partial charges when molecular bonds are broken and the fragments are moved to large distances, even if the proper response would be neutral fragments [16,17]. (ii) QE equalizes electronegativity, while in exact DFT treatments of stretched bonds, electronegativity is not equalized [18]. (iii) The polarizability of polymers (e.g., simple alkanes) growths superlinearly rather than linearly with the degree of polymerization N in the limit of large N [19,12]. (iv) The dielectric permittivity of solids is automatically infinitely large [20]. (v) The only QE-related parameter affecting the skin depth of electrostatic fields is the atomic hardness [20]. (vi) The dipole moment of alcohols growths linearly with the length of the alcohol rather than to level off at constant values when more CH_2 groups are inserted into the tail [21].

Bond-based approaches remedy all these problems when properly parameterized, for example, the correct dissociation limit can be achieved by introducing an appropriate distance dependence of the bond polarizability [17], the dielectric permittivity $\chi = \epsilon_r - 1$ is now finite, (i.e., χ is inversely proportional to the bond hardness [20]), and the dipole of alcohols no longer grows with alcohol length [21]. Yet, new artifacts arise in exclusively bond-based models: (vii) The polarizability per monomer for short chain molecules shows no size dependence, while the correct behavior is an increase of the polarizability with N at small values of N [19]. (viii) The skin depth is zero, i.e., the electrostatic field drops from the value outside a solid to the bulk value within the first surface layer [20]. (ix) It ignores the concept of atomic hardness, which is well motivated from DFT [20]. (x) The values for the bond hardnesses have to be chosen sufficiently large to ensure positive definite Hessians in the charge variables, because atomic hardnesses are neglected. As a consequence, the high-frequency dielectric constant is limited to values only slightly larger than one [20].

SQE does not appear to suffer from any of these issues, because (unlike QE) it can suppress polarizability over long distances through the bond hardness. Unlike AACT, SQE does not require bond hardnesses to be large (or the high-frequency dielectric constants to be small) in order to ensure a positive definite Hessian, because SQE already contains finite atomic hardnesses.

Despite the advantageous features of SQE, it is not clear yet how to treat true ions within SQE (or AACT); any partial atomic charge arises as a sum over split charges that have been locally transferred between two bonded, originally neutral atoms. Thus, so far, any SQE (or AACT) treatment could have only dealt with systems that are locally neutral, and processes as they occur in batteries or in friction-induced contact electrification could not have been described.

To overcome those limitations, it will be necessary to allow the transfer of *integer* charges that are no polarization charges living in a bond. In a closed system, this transfer – or redox reaction – happens between two nearby atoms, in a way such that one atom increases its oxidation state and that of another, nearby atom gets reduced. In a charge equilibration scheme, all dynamic charges or split charges have to re-adjust themselves. This process, which we call backflow, affects the energy balance during the redox reaction. In accordance with the Born-Oppenheimer approximation we assume that the backflow occurs much faster than ionic motion.

As a first step toward understanding the properties of a redox reaction within the respective charge equilibration schemes, we discuss the half reactions first, i.e., study how a molecule or a solid changes its “state” when an integer charge is added to or removed from one of its atoms. The key quantity to be studied in this context is the global chemical hardness κ_g, which has not yet been analyzed within charge equilibration formalisms. It is defined as the second derivative of the energy V_pot with respect to an (elementary) excess charge ΔQ that is placed onto a molecule or a solid. κ_g can be related to the ionization energy I and the electron affinity A [5] through the finite-difference approximation $\kappa_\mathrm{g} = (I - A)/\mathrm{e}^2$, which – in the case of solids – can be associated with the band gap [7, 22,23].

In this work, formal expressions for the global hardness of simple model molecules and model solids are derived within the various charge equilibration formalisms. This is done by assuming that the change of energy of isolated ions with charge can be computed by extrapolating the quadratic expansion around neutral atoms beyond an elementary charge. This approximation may not be accurate enough for practical applications. However, a reparameterization of local terms will mostly affect prefactors. Most generic trends will remain unaltered, such as the functional form of the backflow. Lastly, we discuss in detail how the analytical results can be used for the design of force field-based potentials making it possible to model both equilibrium and non-equilibrium redox reactions.

2 Theory

The energy function in the simplest SQE model for a neutral system reads [11]:

$$V_\mathrm{pot} = \sum_{i,j>i} \frac{\kappa_{\mathrm{s},ij}}{2}\, q_{ij}^2 + \sum_i \left(\frac{\kappa_i}{2}\, Q_i^2 + \chi_i Q_i \right) + V_\mathrm{C}(\{\mathbf{R}, Q\}) \tag{1}$$

with

$$Q_i = \sum_j q_{ij}. \tag{2}$$

In these equations, Q_i represents the charge of atom i, while $q_{ij} \equiv -q_{ji}$ is the “split charge” transferred from atom j to atom i. The electronegativity of atom i is χ_i and κ_i denotes (chemical) hardness. By altering the value of $\chi_i \to \chi_i + \Delta\chi$, one can include effects of an external electrostatic potential at a given site i. $\kappa_{\mathrm{s},ij}$ represents the hardness of the bond connecting atoms i and j. It is assumed to be infinitely large for non-bonded atoms, because no (partial) charge should transfer between two neutral atoms if their orbitals do not overlap, at least as long as external fields are well below dielectric breakthrough strengths. $V_\mathrm{C}(\{\mathbf{R}, Q\})$ summarizes the electrostatic interactions between different charges as a function of their coordinates $\{\mathbf{R}\}$. The set of split charges minimizing Eq. (1) determine the equilibrium charges, from which one would compute electrostatics-related forces via the Hellmann-Feynman theorem.

For simplicity, we use unscreened Coulomb interactions in much of the subsequent treatment. The qualitative conclusions drawn in this work do not depend on the details of V_C, at least as long as one restricts oneself to positive definite Hessians. While the precise values of the atomic charges are certainly sensitive to screening, the functional dependence of the relevant quantity (polarizability) is dominated by the long-range behavior. Similar comments apply to charge- (and later oxidation-state-) dependent corrections that one might want to add to the short-range potential. These corrections do not affect the qualitative conclusions, but only renormalize the free parameters in a quadratic expansion of $V(\{\mathbf{Q}\})$ around the minimum.

Regular QE is the limiting case of SQE in which all bond hardnesses are set to zero. Even bond hardnesses of non-bonded atoms would have be set to zero in an SQE treatment of regular QE, unless local charge constraints were imposed by hand, as was done for individual water molecules in the simulation of liquid water in Refs. [24, 25]. The AACT model is the limit of SQE in which the bond hardnesses are finite but the atomic hardnesses are set to zero.

An external excess charge ΔQ_i can be added to atom i by substituting the charge Q_i in Eq. (1) according to:

$$Q_i = \sum_j q_{ij} + \Delta Q_i. \tag{3}$$

This addition of excess charge induces a backflow in the split charges, which makes Q_i move away from integer values and also affects the total energy. Formally, ΔQ_i is infinitesimally small, however, we assume implicitly that ΔQ_i is an integer multiple of an elementary charge. In the language of chemistry, adding an integer positive charge corresponds to oxidation, while removing one reflects reduction.

It is clear that only integer charges can be added to a real system, at least if one wants the charge-adding device to no longer interfere with the molecule or solid of interest after the charge was added. It is less obvious that one should simply assign this excess charge to an individual atom, or in the words of chemistry, it is not clear that an atom has a well-defined oxidation state. For the time being, let us assume that assigning (integer) oxidation states is meaningful. One can then analyze what ionization energies and electron affinities result in different charge equilibration schemes. However, we will also analyze what values would be obtained for I and A if this excess charge were distributed evenly over the atoms.

The following (operational) definition for the chemical hardness will be used:

$$\kappa_g = \frac{\partial^2 V_{\text{pot}}}{\partial \Delta Q^2}, \tag{4}$$

where the boundary condition is that the set of split charges minimizes V_{pot} at each given value of $\{\Delta Q_i\}$. Since our energy expression is quadratic by construction, this definition of κ_{g} and the finite-difference definition of $\kappa_{\text{g}} = I - A$ coincide. In more refined treatments, for example if the charge of an atom explicitly affected parameters of the force field, as for example in breathing-shell models of ionic solids [26], the two definitions for κ_{g} lead to slightly different values.

In the following Sections we evaluate Eq. (4) for a diatomic molecule and a simple cubic crystal in order to elucidate the influence that the microscopic terms, such as atomic hardness, bond hardness, and Coulomb interactions have on the effective hardness of a system as well as on other phenomenological properties. This includes a quantitative analysis of the NaCl molecule.

2.1 Diatomic molecule

We start our discussion with the simplest possible model from which one can ascertain essentially all qualitative conclusions drawn in this work, i.e., we consider a heteronuclear diatomic molecule. The external charge is going to be placed onto atom 1. The split charge q_{12} is simply going to be written as q and $\Delta\chi \equiv \chi_{12} \equiv \chi_1 - \chi_2$. The distance between the two atoms is denoted by a. V_{pot} then reads:

$$\begin{aligned} V_{\text{pot}} = {} & \frac{\kappa_1}{2}(\Delta Q + q)^2 + \frac{\kappa_2}{2}(-q)^2 + \frac{\kappa_{\text{s}}}{2}q^2 \\ & + \Delta\chi \cdot q + \chi_1 \cdot \Delta Q + \frac{J_{\text{C}}}{2}(\Delta Q + q)(-q), \end{aligned} \tag{5}$$

where in the case of regular Coulomb interactions J_{C} can be calculated with

$$J_{\text{C}} = \frac{1}{2\pi\epsilon_0 a}. \tag{6}$$

The split charge can now be determined by demanding that $\mathrm{d}V_{\text{pot}}/\mathrm{d}q = 0$, leading to:

$$q = -\frac{(\kappa_1 - J_{\text{C}}/2) \cdot \Delta Q + \Delta\chi}{\kappa_1 + \kappa_2 + \kappa_{\text{s}} - J_{\text{C}}}. \tag{7}$$

As usual, one requires the denominator to be positive, because this ensures that V_{pot} is minimized and not maximized with respect to q. Eq. (7) can now be inserted into Eq. (5) and the result be sorted into powers of ΔQ. This leads to

$$V_{\text{pot}}(\Delta Q) = \frac{\kappa_g}{2} \cdot \Delta Q^2 + \chi \cdot \Delta Q + V_{\text{pot}}(0), \tag{8}$$

where

$$\kappa_g = \frac{\kappa_1 \cdot (\kappa_2 + \kappa_{\text{s}}) - (J_{\text{C}}/2)^2}{\kappa_1 + \kappa_2 + \kappa_{\text{s}} - J_{\text{C}}} \tag{9}$$

is the global hardness,

$$\chi = \frac{(\kappa_2 + \kappa_{\text{s}} - J_{\text{C}}/2) \cdot \chi_1 + (\kappa_1 - J_{\text{C}}/2) \cdot \chi_2)}{\kappa_1 + \kappa_2 + \kappa_{\text{s}} - J_{\text{C}}} \tag{10}$$

is the global electronic chemical potential, and

$$V_{\text{pot}}(\Delta Q = 0) = -\frac{1}{2} \cdot \frac{\Delta\chi^2}{\kappa_1 + \kappa_2 + \kappa_{\text{s}} - J_{\text{C}}} \tag{11}$$

is the energy associated with the split charge for a neutral molecule in which both atoms have oxidation state zero. A variety of instructive limits shall now be discussed.

2.1.1 Heteronuclear QE molecule

From Eq. (9), one can see that κ_g is symmetric in the indices 1 and 2 if $\kappa_{\text{s}} = 0$, which implies that the global hardness is independent of which atom ΔQ has been placed on. As a matter of fact, none of the terms, including Q_1 and Q_2, depend on to which atom the excess charge had been donated. V_{pot} becomes particularly straightforward to interpret (see also Ref. [27]) if one neglects the Coulomb interaction in a heteronuclear QE molecule ($\kappa_{\text{s}} = 0$),

$$V_{\text{pot}} = \frac{1}{2}\left(\frac{1}{\kappa_1} + \frac{1}{\kappa_2}\right)^{-1} \cdot \Delta Q^2 + \frac{\kappa_2\chi_1 + \kappa_1\chi_2}{\kappa_1 + \kappa_2} \cdot \Delta Q. \tag{12}$$

One can recognize that the electronic chemical potential is a (weighted) average of the electronic chemical potential of the individual atoms. More importantly, the inverse atomic hardnesses add, similar to the way how capacitances or springs add when coupled in series. This series coupling of atomic hardnesses is at the root of a vanishing global hardness in many-atom QE molecules or QE solids. More generally speaking, it is at the root of why a QE material is metallic. Many attempts to make QE non-metallic, such as introducing screening for electronegativity differences, therefore fail. A successful attempt to construct the correct dielectric susceptibility is necessarily based on finding the proper Hessian for the charge variables.

We will see later that it matters in SQE to which atom the excess charge was added. Thus, there is a qualitative difference between these two methods in terms of their response to an external excess charge, which already becomes apparent for a diatomic molecule. In order to ascertain a qualitative difference between QE and SQE in terms of their dielectric susceptibility, it is necessary to study system-size effects.

2.1.2 Homonuclear AACT model

When neglecting interatomic charge interaction in a diatomic, homonuclear AACT molecule ($\chi \equiv \chi_1$; $\chi_{12} = 0$), there is no incentive to redistribute the charge, because $\kappa_\mathrm{s} q^2/2$ is the only remaining summand to the net energy that depends on q. Once a finite (positive) value of J_C is considered, the situation changes. However, in contrast to chemical or physical intuition, $q = J_\mathrm{C} \Delta Q / \{2 \cdot (\kappa_\mathrm{s} - J_\mathrm{C})\}$ turns out to be of the same sign as ΔQ given that the model is positive definite in q. One must conclude that backflow has the wrong sign in AACT.

When minimizing V_pot in AACT, it is easy to see that the homonuclear reduces the net energy according to

$$V_\mathrm{tot} = -\frac{1}{2} \cdot \frac{(J_\mathrm{C}/2)^2}{\kappa_\mathrm{s} - J_\mathrm{C}} \cdot \Delta Q^2 + \chi \cdot \Delta Q, \tag{13}$$

which means that the hardness is negative (despite V_pot being positive definite in q). Consequently, charge would diverge on atoms in the grand canonical ensemble. This result, which would be similar for heteronuclear molecules, can certainly be branded as pathological, just like the negative backflow.

The origin of this counterintuitive behavior is that one can add charge to an atom without energy penalty. Thus, if we added a charge +1 to an atom in a molecule or in a solid consisting of originally neutral atoms and removed a charge from another atom, one would not have to pay any penalty energy, yet Coulomb interaction energy would be gained. This property of AACT is at the origin of the (unphysical) band crossing of conduction and valence band when applied to solid as will be seen later.

2.1.3 Homonuclear SQE molecule

In the case of the homonuclear molecule, one can set $\kappa_\mathrm{a} \equiv \kappa_1 = \kappa_2$, and in the absence of an external electric field $\Delta\chi = 0$. The global hardness for the homonuclear SQE molecule turns out less than that of the individual atoms, at least as long as V_pot is expanded around neutral atoms, but for any realistic parameterization it should turn out positive. In Fig. 1, it is shown how κ_g changes with κ_a and κ_s in the homonuclear SQE model and how QE and AACT formally arise as a limiting case of SQE.

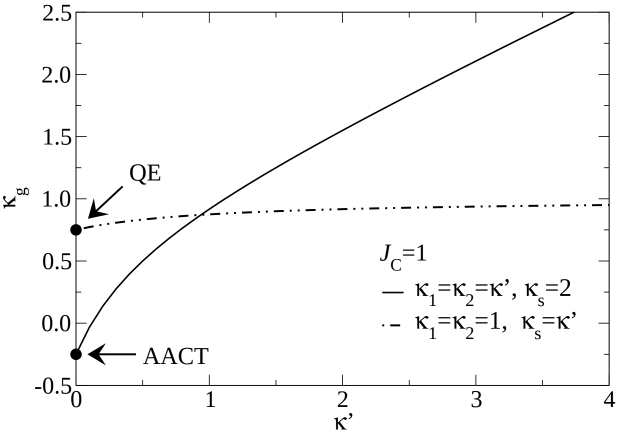

Fig. 1. The hardness of a homonuclear molecule in the SQE model for different parameterizations. In realistic SQE parameterizations, atomic hardnesses exceed bond hardnesses so that κ_g(SQE) turns out positive.

When adding an excess charge ΔQ onto atom 1, its charge can be written as

$$Q_1 = \frac{1}{2}\left(1 + \frac{\kappa_s}{2\kappa_a + \kappa_s - J_C}\right)\Delta Q. \tag{14}$$

Thus, Q_1 is greater than $\Delta Q/2$ and therefore exceeds Q_2. At the same time, Q_1 is less than ΔQ. The reason is that $2 \cdot \kappa_a$ should in most cases be greater than both J_C and κ_s. This is because κ_a represents the self-interaction of an electron on an atom, while κ_s and J_C reflect interactions of orbitals centered on different atoms. In the Section on solids, we further substantiate why κ_s should be smaller than κ_a.

For the homonuclear diatomic molecule, one may notice the following sequence of inequalities – assuming that κ_a and κ_s are both positive in SQE:

$$\frac{Q_1(\text{QE})}{\Delta Q} = \frac{1}{2} < \frac{Q_1(\text{SQE})}{\Delta Q} < 1 < \frac{Q_1(\text{ACCT})}{\Delta Q}. \tag{15}$$

Thus, the three approaches result in three fundamentally different responses when an excess charge ΔQ is added to atom 1. This is demonstrated visually in Fig. 2.

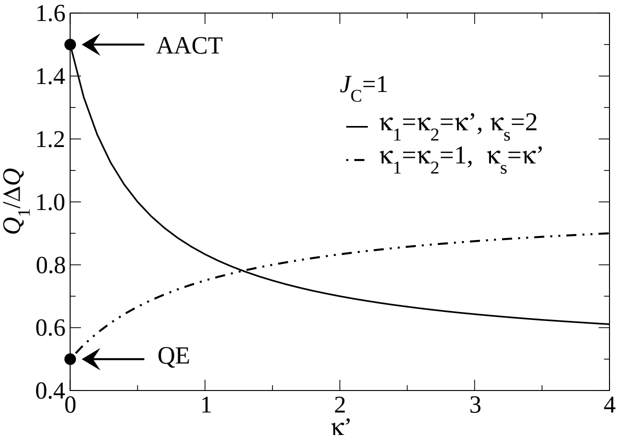

Fig. 2. The final charge Q_1 of an atom in a homonuclear SQE molecule to which an excess charge ΔQ is added. Different parameterizations are considered. Atomic hardnesses exceed bond hardnesses in realistic SQE parameterizations so that $1/2 < Q_1(\text{SQE}) < 1$.

An important observation for the SQE treatment of homonuclear molecules is that the electronic chemical potential of the molecule is identical to that of each individual atom, while the hardness, which remains positive for reasons mentioned earlier, is reduced.

As a consequence of κ_g being less than κ_a, the (global) electron affinity of a homonuclear SQE molecule

$$A_g = \chi \cdot \text{e} - \kappa_g \cdot \text{e}^2/2 \tag{16}$$

is increased with respect to that of an individual atom (since κ_g is less than κ_a), while its (global) ionization energy

$$I_g = \chi \cdot \text{e} + \kappa_g \cdot \text{e}^2/2 \tag{17}$$

is decreased. This result, which requires some analysis of Eq. (9) under the assumption of $\kappa_\mathrm{a} > J_\mathrm{C}$, will be important to keep in mind when addressing the question of how to treat true ions in SQE.

In realistic treatments of molecular hardness, significant corrections will certainly be necessary, in particular when a closed-shell molecule is formed. For example, it is well established that the hardness of a molecule correlates with its stability [28]. We might want to reflect this by choosing a large value of κ_s for strong chemical bonds and by potentially adding further bond-order dependent corrections. However, at this point it is important to investigate the trends that each charge equilibration models predicts without further refinement before a tedious parameterization is conducted.

A non-homogeneous distribution of the excess charge in a homonuclear molecule violates the symmetry of the Hamiltonian. It may be tempting to reestablish the symmetry by hand by distributing $\varDelta Q$ evenly over the two atoms and/or by introducing split charges between atoms and a fictitious reservoir. Neither approach will be a good idea for a variety of reasons but mainly because either approach shortcuts the bond hardness terms – even when two atoms are far away from one another. The investigated system would then automatically be metallic just as in the original QE method.

In order to reestablish symmetry, we can treat the oxidation state of an atom as a dynamic variable by introducing discrete trial moves mimicking an electron transfer reaction. Concretely, one can decrease Q_1 by an elementary charge $\varDelta Q$ and increase Q_2 by the same amount. The net energy balance in the case of the considered redox self-exchange reaction would be zero and both atoms would have an average oxidation state of 1/2 in thermal equilibrium. Yet, at each instance of time, the oxidation state of an atom would be an integer number.

2.2 Case study for the NaCl molecule

The treatment presented in the previous Section makes it possible to compare the microscopic parameters of the SQE model to a variety of experimentally measurable observables. Such a quantitative analysis based on the NaCl molecule is conducted in this Section. The goal is once more to ascertain trends rather than to produce accurate numbers. This is why we abstain from adjusting the bond-related parameters κ_s and J_C when the oxidation states of atoms changes.

Almost all "force field" parameters in the SQE model are those related to the Na and Cl atoms. The respective values in Ref. [29] are: $\chi_\mathrm{Na} = 2.73$ eV, $\kappa_\mathrm{Na} = 5.82$ eV, $\chi_\mathrm{Cl} = 8.53$ eV, and $\kappa_\mathrm{Cl} = 9.82$ eV. The coupling at the experimental NaCl bond length, $a^0_\mathrm{NaCl} = 2.36$ Å, would be $J_\mathrm{pC} = e/(2\pi\epsilon_0 \cdot 2.36\text{ Å}) = 12.2$ eV for the bare Coulomb potential. However, for the analysis of the molecule at its ideal bond length, we use the value for the screened Coulomb interaction, $J^0_\mathrm{C} = 7.11$ eV, instead. We augment the set of parameters by a bond hardness of $\kappa_\mathrm{NaCl} = 8$ eV, which is close to the band gap of solid rocksalt. We justify this choice in the Section on solids. Lastly, we assume that the electron affinity of the chlorine anion is zero and use a second ionization energy of the sodium atom of 47 eV.

2.2.1 Expansion around neutral atoms

We first characterize the molecule for the case in which the oxidation states of both atoms are zero. Using two superscripts to label the oxidation states of Na and Cl atoms, respectively, $Q_{\mathrm{Na}}^{00} = q$ becomes by Eq. (7)

$$Q_{\mathrm{Na}}^{00} = \frac{-\chi_{\mathrm{NaCl}}}{\kappa_{\mathrm{QE}} + \kappa_{\mathrm{NaCl}}}, \tag{18}$$

where

$$\kappa_{\mathrm{QE}} = \kappa_{\mathrm{Na}} + \kappa_{\mathrm{Cl}} - J_{\mathrm{C}}^{0}. \tag{19}$$

The potential energy associated with the '00' oxidation state is

$$V_{\mathrm{pot}}^{00} = \frac{-\chi_{\mathrm{NaCl}}^{2}}{2 \cdot (\kappa_{\mathrm{QE}} + \kappa_{\mathrm{NaCl}})}. \tag{20}$$

The following numerical values result for the QE and SQE approaches: $Q_{\mathrm{Na}}^{00}(\mathrm{QE}) = 0.68$ and $Q_{\mathrm{Na}}^{00}(\mathrm{SQE}) = 0.35$. The QE value is much closer to the charge of the Na atom that one would deduce from the experimental dipole moment of 9.0 D, namely $Q_{\mathrm{Na}}^{\mathrm{exp}} \approx 0.8$. This, however, is notsignificant, because the oxidation state '00' is not the energetically most favorable state in SQE.

One can repeat the preceding analysis for an oxidation state '+−'. In this case, the potential energy to minimize with respect to q is:

$$V_{\mathrm{pot}}^{+-}(q) = \frac{\kappa_{\mathrm{QE}}}{2}(1+q)^2 + \chi_{\mathrm{NaCl}} \cdot (1+q) + \frac{\kappa_{\mathrm{NaCl}}}{2} \cdot q^2, \tag{21}$$

which yields

$$Q_{\mathrm{Na}}^{+-} = \frac{-\chi_{\mathrm{NaCl}} + \kappa_{\mathrm{NaCl}}}{\kappa_{\mathrm{QE}} + \kappa_{\mathrm{NaCl}}}. \tag{22}$$

Within the QE approach, $Q_{\mathrm{Na}}^{+-}(\mathrm{QE})$ remains unaltered, because in QE it does not matter what atom an excess charge is put on. In contrast, $Q_{\mathrm{Na}}^{+-}(\mathrm{SQE}) = 0.83$ has increased by 0.48 elementary charges as compared to the '00' oxidation state and now compares nicely to the experiment-based estimate of 0.8.

The value of the potential energy for the '+−' oxidation state turns out to be

$$V_{\mathrm{pot}}^{+-} = \frac{\kappa_{\mathrm{NaCl}} \cdot (\kappa_{\mathrm{QE}} + 2\chi_{\mathrm{NaCl}}) - \chi_{\mathrm{NaCl}}^{2}}{2 \cdot (\kappa_{\mathrm{QE}} + \kappa_{\mathrm{NaCl}})}. \tag{23}$$

Thus, the energy to be gained by transitioning from '00' to '+−' is

$$\Delta E_{\mathrm{redox}} = \frac{-\kappa_{\mathrm{NaCl}} \cdot (\kappa_{\mathrm{QE}} + 2\chi_{\mathrm{NaCl}})}{2 \cdot (\kappa_{\mathrm{QE}} + \kappa_{\mathrm{NaCl}})}. \tag{24}$$

The numerical value for $\Delta E_{\mathrm{redox}}(\mathrm{SQE}) = 0.74$ eV must be compared to the first electronic excitation energy of NaCl, which was computed to be 3.28 eV within a DFT calculation [30]. Thus, an expansion aroung neutral atoms produced a value for $\Delta E_{\mathrm{redox}}(\mathrm{SQE})$ that is too small by a factor of four. To improve this situation, one either has to use unrealistic values for J_{C} or κ_{s}, or alternatively, to expand around the ionic state when computing V_{pot}^{+-}.

Within a given calibration, the redox reaction should occur as soon as $\kappa_{\mathrm{QE}} + 2\chi_{\mathrm{NaCl}}$ is less than zero. This would then be a radiation free reaction, although the charges would change discontinuously during the reaction. To estimate the value where this happens, we use the pure Coulomb potential. The condition for the "redox distance", a_{redox}, then reads:

$$\kappa_{\mathrm{Na}} + \kappa_{\mathrm{Cl}} - J_{\mathrm{pC}}(a_{\mathrm{NaCl}}^{0}) \frac{a_0}{a_{\mathrm{redox}}} + 2\chi_{\mathrm{NaCl}} = 0, \tag{25}$$

which can be solved to yield $a_{\mathrm{redox}} = 7.3$ Å.

We finally add excess charges to the neutral molecule. Given the formulas in Sec. 2.1, one obtains: $\kappa_{\mathrm{g,Cl}}(\mathrm{SQE}) = 8.9$ eV and $\kappa_{\mathrm{g,Na}}(\mathrm{SQE}) = 7.0$ eV. In the QE model, it does not matter if we place charge on Cl or on Na, and thus $\kappa_{\mathrm{g}}(\mathrm{QE}) = 5.2$ eV takes the same value for both atoms. As argued before, the hardness in the QE approach turns out to be smaller than in SQE, no matter which atom receives the excess charge in the SQE model. If, however, $\kappa_{\mathrm{g}}(\mathrm{SQE})$ is computed by considering the oxidation states '+0' and '0−' for the ions, the latter claim no longer needs to hold. Finally, the electronegativities in QE $\chi_{\mathrm{g}}(\mathrm{QE}) = 4.4$ eV lies in between the values $\chi_{\mathrm{g,Cl}}(\mathrm{SQE}) = 6.3$ eV, $\chi_{\mathrm{g,Na}}(\mathrm{SQE}) = 3.5$ eV.

Once the values for χ_{g} and κ_{g} are known, one can calculate the molecular ionization energies and electron affinities. In the QE approach, no ambiguity exists regarding what atom receives the excess charge. In SQE, the smallest ionization energy is obtained by adding a positive charge to the sodium. Adding a negative charge to the chlorine maximizes the electron affinity. Thus,

$$\begin{aligned} A_g(\mathrm{SQE}) &= \chi_{\mathrm{g,Cl}}(\mathrm{SQE}) - \kappa_{\mathrm{g,Cl}}(\mathrm{SQE})/2 - \Delta E_{\mathrm{redox}} \\ &= 1.87 \text{ eV} \\ I_g(\mathrm{SQE}) &= \chi_{\mathrm{g,Na}}(\mathrm{SQE}) + \kappa_{\mathrm{g,Na}}(\mathrm{SQE})/2 + \Delta E_{\mathrm{redox}} \\ &= 7.02 \text{ eV} \\ A_g(\mathrm{QE}) &= \chi_{\mathrm{g}}(\mathrm{QE}) - \kappa_{\mathrm{g}}(\mathrm{QE})/2 = 1.96 \text{ eV} \\ I_g(\mathrm{QE}) &= \chi_{\mathrm{g}}(\mathrm{QE}) + \kappa_{\mathrm{g}}(\mathrm{QE})/2 = 6.88 \text{ eV}. \end{aligned}$$

The ionization energies are only ≈ 25% smaller than the desired value of $I_g(\mathrm{DFT}) = 9.3$ eV [30]. The agreement is surprisingly good, given that $Q_{\mathrm{Na}}^{+-}(\mathrm{SQE})$ turns out to slightly exceeded +1. The deviation from $A_g(\mathrm{DFT}) = 0.87$ eV [30], are, however, quite substantial. This could have been expected, because the NaCl molecule forms a closed electron shell and our estimate for the propensity to attract additional charge was based on electronegativities of atoms with open shells. Both numbers can easily be improved, just as $\Delta E_{\mathrm{redox}}$ before, by assigning sensibly chosen ionic hardnesses and electronegativities. This is shown next.

2.2.2 Expansion around ions

After an atom has changed its oxidation state, it is meaningful to expand the energy around that given oxidation state rather than around the neutral atom [31]. For the '+−' oxidation state of the NaCl atom, one would then have to find the value of q that minimizes

$$\begin{aligned} V_{+-}(q) = \frac{1}{2}&(\kappa_{\mathrm{Na}^+} + \kappa_{\mathrm{Cl}^-} + \kappa_{\mathrm{s}} - J_{\mathrm{C}}) \cdot q^2 \\ &+(\chi_{\mathrm{Na}^+} - \chi_{\mathrm{Cl}^-} - J_{\mathrm{C}}) \cdot q + I_{\mathrm{Na}} - A_{\mathrm{Cl}}. \end{aligned} \quad (26)$$

Similar potential energy functions to be minimized can be constructed for the '+0' and the '0−' oxidation states of the molecule. Proceeding as in Sect. 2.2.1 and calibrating the parameters as stated at the beginning of Sect. 2.2, quite reasonable numbers can be obtained. The ionization energy now is $I_{\mathrm{g}}(\mathrm{SQE}) = 8.5$ eV and $I_{\mathrm{g}}(\mathrm{QE}) = 7.0$ eV, which compares well with the DFT value of 9.3 eV. The error in $\Delta E_{\mathrm{redox}}(\mathrm{DFT}) = 3.28$ eV has reduced dramatically, i.e., $\Delta E_{\mathrm{redox}}(\mathrm{SQE}) = 3.8$ eV and $\Delta E_{\mathrm{redox}}(\mathrm{QE}) = 3.6$ eV. The correction in the electronegativity of the molecule has the correct trend, although it overshoots to slightly negative values, i.e., $\chi_{\rm g}(\rm SQE) = -0.88$ eV and $\chi_{\rm g}(\rm QE) = -0.42$ eV. The only disimprovement is a considerably reduced charge on the sodium, specifically $Q_{\rm Na}(\rm SQE) = 0.62$ and $Q_{\rm Na}(\rm QE) = 0.54$.

It is easily possible to improve the results for $Q_{\rm Na}$ and $\chi_{\rm g}$ by using higher-order polynomials for $V_{\rm Na}(Q)$ and $V_{\rm Cl}(Q)$ without deteriorating the agreement for $\mathit{\Delta} E_{\rm redox}$ and $I_{\rm g}$. However, this would be fine-tuning that we want to leave for another study, in which transferability shall be tested. There, we will also argue in detail why the stated approach is *not* in contradiction to the finding by DFT that the derivative of *isolated* fragments (atoms or molecules) are discontinuous at integer values of the charge [32, 33]. Here, it shall suffice to say that isolated SQE fragments can only acquire integer charges in their ground-state, while the response of molecules and solids to external electrostatic fields is continuous, except at instability points where a redox reaction occurs. The latter would not be the case if we translated the DFT insight in a naive way and made the atomic expressions for $V(Q)$ piecewise linear.

2.3 Periodic systems

2.3.1 Analytical considerations

In order to identify the generic properties of excess charges in polymers and solids, we analyze periodically repeated systems, as they are amenable to significant simplification of the underlying mathematics without compromising the validity of the conclusions for more general situations: charges and split charges associated with different wave vectors $\mathbf{k}$ decouple due to translational invariance – at least as long as one restricts oneself to expressions that are quadratic in charges and split charges. For a monatomic crystal, $V_{\rm pot}$ therefore reads as follows:

$$V_{\rm pot} = N \cdot \sum_{\mathbf{k}} \left\{ \sum_{\alpha\beta} \frac{\tilde{\kappa}_{s,\alpha\beta}(\mathbf{k})}{2} \tilde{q}^*_\alpha(\mathbf{k}) \tilde{q}_\beta(\mathbf{k}) + \frac{\kappa_a + \tilde{J}_C(\mathbf{k})}{2} |\tilde{Q}(\mathbf{k})|^2 + \tilde{\chi}(\mathbf{k}) \tilde{Q}^*(\mathbf{k}) \right\}. \quad (27)$$

Tildes indicate the Fourier transforms of the quantities that were introduced earlier. We define the Fourier transform of a function f defined on a lattice via $\tilde{f}(\mathbf{k}) = (1/N) \cdot \sum_{n=1}^{N} f_n \exp(i\mathbf{k} \cdot \mathbf{R}_n)$, where n runs over all N elementary cells (atoms), and $\mathbf{R}_n$ is the coordinate of the lattice site.

More than one split charge resides on each lattice site, except for the homatomic, linear chain with nearest-neighbor coupling, so that the q_{ij} turn into $\tilde{q}_\alpha(\mathbf{k})$ and $\kappa_{\rm s}$ into a matrix $\tilde{\kappa}_{s,\alpha\beta}$. The Greek indeces run from 1 to half the number of neighbors with which a central atom shares a split charge. For example in a simple cubic system, one assigns one split charge between the central atom and nearest neighbors that are displaced by one lattice constant a in x or y or z direction, and are consequently labeled in reciprocal space as $\tilde{q}_1(\mathbf{k})$, $\tilde{q}_2(\mathbf{k})$, and $\tilde{q}_3(\mathbf{k})$, respectively. Coupling to next nearest neighbors requires six more split charges per atom in real space, and the dimensions of $\tilde{q}$ and $\tilde{\kappa}_s$ has to be expanded accordingly. None of the conclusions drawn in this Section is affected in a qualitative fashion if we introduced next-nearest coupling or crystals with basis so that we content ourselves with the simplest possible case, that is, a simple cubic solid, for which

$$\tilde{\kappa}_{s,\alpha\beta}(\mathbf{k}) = \kappa_{\mathrm{s}} \cdot \delta_{\alpha\beta}. \tag{28}$$

Adding an extra charge to an individual atom can be done as in the treatment of molecules, except that one should subtract a charge-balancing background in a periodic system to keep the Coulomb energy from diverging. Thus, if we place an excess charge $\mathit{\Delta} Q$ onto an atom (whose position will define the center of the coordinate system), the analogue to Eq. (3) becomes

$$\tilde{Q}(\mathbf{k}) = \tilde{Q}_s(\mathbf{k}) + \mathit{\Delta}\tilde{Q}(\mathbf{k}), \tag{29}$$

where $\tilde{Q}_s$ indicates charge resulting from charge transfer between atoms, and

$$\mathit{\Delta}\tilde{Q}(\mathbf{k}) = \frac{1}{N} \cdot (1 - \delta_{\mathbf{k},0}) \cdot \mathit{\Delta} Q \tag{30}$$

represents the externally added charge.

Minimization of V_{pot} can be achieved by requiring that $\partial V_{\mathrm{pot}}/\partial \tilde{q}^*_\alpha(\mathbf{k})$ be zero. In order to keep the treatment as simple as possible, it is easiest to use the continuum limit for a simple cubic lattice, in which one can exploit a result of Ref. [20]:

$$\tilde{Q}_s(\mathbf{k}) = \sum_\alpha i(ak_\alpha)\tilde{q}_\alpha(\mathbf{k}). \tag{31}$$

Thus, minimization of V_{pot} demands that for each $\mathbf{k}$ and α, the equation

$$i(ak_\alpha)\left[\tilde{\chi}(\mathbf{k}) + \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}\mathit{\Delta}\tilde{Q}(\mathbf{k})\right] = \sum_\beta \left[\kappa_s \cdot \delta_{\alpha\beta}(\mathbf{k}) + a^2 k_\alpha k_\beta \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}\right]\tilde{q}_\beta(\mathbf{k}). \tag{32}$$

holds. This expression can be diagonalized with the ansatz

$$\tilde{q}_\alpha(\mathbf{k}) = -i\frac{(ak_\alpha)\tilde{Q}_s(\mathbf{k})}{(ak)^2}, \tag{33}$$

resulting in

$$\tilde{Q}_s(\mathbf{k}) = -\frac{\tilde{\chi}(\mathbf{k}) + \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}\mathit{\Delta}\tilde{Q}(\mathbf{k})}{\kappa_s/(ak)^2 + \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}}. \tag{34}$$

The change in potential energy due to an excess charge can be calculated by inserting Eq. (34) into Eq. (27). The result arises as a sum over $\mathbf{k}$-dependent terms of the form

$$V_{\mathrm{pot}}(\mathbf{k}) = \frac{1}{2} \cdot \kappa_g(\mathbf{k}) \cdot \mathit{\Delta}\tilde{Q}(\mathbf{k})^2. \tag{35}$$

with

$$\kappa_g(\mathbf{k}) = \frac{\kappa_{\mathrm{s}} \cdot (ak)^2 \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}}{\kappa_{\mathrm{s}} + (ak)^2 \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}} \tag{36}$$

In order to proceed further, it is necessary to insert a model for the Coulomb interaction $\tilde{J}_C(\mathbf{k})$. This term can have different functional forms, depending on the precise nature of Coulomb screening at short distances. The important long wavelengths, however, will not be affected by short-range screening. It will therefore suffice to include the leading-order terms in $\tilde{J}_C(\mathbf{k})$. Nevertheless one should not truncate already at the continuum limit, but include the lowest-order discretization corrections in $\tilde{J}_C(\mathbf{k})$ so that a charge-density wave at $\mathbf{k} = (\pi/a)(1,1,1)$ is energetically beneficial; in other words, we would want the Madelung constant for the rocksalt structure to be positive and not negative. In Fig. 1 of Ref. [11] it was demonstrated that

$$\tilde{J}_C(\mathbf{k}) = \frac{1 - \alpha(ak)^2}{(\epsilon_0 \cdot a) \cdot (ak)^2} \tag{37}$$

is a reasonable approximation for $\tilde{J}(\mathbf{k})$ in the first Brillouin zone (BZ) of a simple cubic solid with $\alpha = 0.2257(8)$. The largest error in $\tilde{J}_C$ within the first BZ occurs at $\mathbf{k} = (\pi/a)(1,1,1)$, where one would predict the rocksalt Madelung constant to be 2.39 instead of the correct value near 1.75.

Using the specific choice for $\Delta\tilde{Q}(\mathbf{k})$ from Eq. (30), one obtains for the global hardness:

$$\kappa_g = \frac{\partial^2 V_{\mathrm{pot}}}{\partial \Delta Q^2} = \frac{1}{N} \sum_{\mathbf{k}\in 1.\mathrm{BZ}} \kappa_g(\mathbf{k}) \tag{38}$$

This term converges to a unique value of κ_g in the thermodynamic limit. It is unfortunate that this sum does not simplify more even when the sum over $\mathbf{k}$ vectors is replaced with an integral. One would have to make a variety of approximations. The two simplest limiting cases are that either $(ak)^2 \cdot \epsilon_0 \cdot a \cdot \kappa_a$ much exceeds $\tilde{J}_c(\mathbf{k})$ or, alternatively, $1/\epsilon_0 a$ is much greater than $(\kappa_a - \alpha/\epsilon_0 a)(ak)^2$. Both cases correspond to k-point sampling with one point in the Γ point and yield

$$\kappa_g \approx \kappa_s. \tag{39}$$

Hence, κ_{s} does not only control the dielectric permittivity of a solid but also its electronic hardness. Since the latter can be related to the band gap [22], SQE produces a dielectric permittivity that is roughly inversely proportional to the band gap. We will substantiate this claim by conducting a more detailed analysis next.

2.3.2 Interpretation of analytical results

In this Section, we discuss the implications of the analytical considerations on the periodic systems in the context of the three charge equilibration approaches. First, let us consider Eq. (35), which is the energy associated with an external charge in reciprocal space. The corresponding hardness $\kappa_g(\mathbf{k})$ arises in analogy to the series coupling of two springs, or two hardnesses, namely the bond hardness and $\kappa_{\mathrm{aC}}(\mathbf{k}) \equiv (ak)^2 \left\{\kappa_a + \tilde{J}_C(\mathbf{k})\right\}$ term. The latter could be called a wavelength dependent, Coulomb-corrected atomic hardness. Thus, in order to produce a band gap, or positive values of $\kappa_g(\mathbf{k})$ everywhere in the first B.Z., both $\kappa_{\mathrm{aC}}(\mathbf{k})$ and κ_a must be positive.

Adding a charge to a QE crystal at non-zero wavevector happens at a zero energy balance, because κ_{s} and thus $\kappa_g(\mathbf{k} \neq 0)$ is zero in QE. Note also that the backflow exactly compensates the externally added charge, as one can see from Eq. (34). Energy would only increase in a *finite* system. There, charge would accumulate near the surfaces. Conducting similar calculations as those presented in Ref. [20], it is straightforward to obtain a charge density that decays exponentially from the surface with a correlation length of $a \cdot \sqrt{\epsilon_0 \cdot a \cdot \kappa_a}$.

In the AACT model, the situation is even worse than in QE: $\kappa_g(\mathbf{k})$ is not only zero but *negative* for the wave numbers that have a negative $\tilde{J}(\mathbf{k})$. For example, if we populate a monatomic solid in the AACT model at $\mathbf{k} = (\pi/a)\cdot(1,1,1)$, i.e., such that the "sodium" positions in the simple cubic lattice are positively and the "chlorine" positions negatively charged, then no energy penalty would have to be paid by the AACT hardness terms. Yet, we would have gained Coulomb energy. In the language of band structure, this means that valence and conduction bands cross, which is unphysical. Given Eq. (37) and the value of α obtained in Ref. [20], the crossing would occur at wave vector of magnitude $k \approx 1/(0.2258 \cdot a)$, i.e., well within the first B.Z. As shown below, screening barely changes this result as long as κ_a is set to zero.

In order to obtain physically meaningful hardnesses for dielectric materials, $\kappa_{\rm s}$ must be positive, and κ_a must exceed $J_{\rm C}(\mathbf{k})$ for every $\mathbf{k}$. This last condition happens to be identical to that of a positive definite Hessian with respect to atomic charges in the original QE model; κ_a must exceed a threshold hardness, whose precise value depends on the screening of the Coulomb corrections. Thus, one should not use $\kappa_{\rm s}$ to construct a positive definite Hessian in the split charges, or one risks to have band crossing as it occurs in AACT. For the simple-cubic solid without screening, we would have to request that $\kappa_a(\epsilon_0 \cdot a) > \left\{\alpha \cdot (ak_{\rm max})^2 - 1\right\}/(ak_{\rm max})^2$ with $(a\cdot k_max)^2 = 3\pi^2$, which would result in rather large $\kappa_a > 12$ eV if we use the nearest-neighbor NaCl distance in a rocksalt solid for a. It yet seems as if the requirement of a positive $\kappa_{aC}(\mathbf{k})$ is usually satisfied; elements with small values of κ_a will have large screening corrections and vice versa. A semi-quantitative analysis of the effect of screening is given next.

Let us estimate typical values for $\tilde{\kappa}_g(\mathbf{k})$ real materials by considering a variety of limiting cases. As before, the unit of charge will be the elementary charge so that hardnesses are stated in eV rather than in V/e.

(i) $\kappa_{\rm a} = 8$ eV, $\kappa_{\rm s} = 0$ eV, QE / SQE metal
(ii) $\kappa_{\rm a} = 8$ eV, $\kappa_{\rm s} = 1$ eV, SQE (medium band gap)
(iii) $\kappa_{\rm a} = 8$ eV, $\kappa_{\rm s} = 8$ eV, SQE (large band gap)
(iv) $\kappa_{\rm a} = 0$ eV, $\kappa_{\rm s} = 8$ eV, AACT.

The atomic hardness of 8 eV is a typical value for atoms, i.e., it is close to the mean value of $\kappa_{\rm a}$(Na) and $\kappa_{\rm a}$(Cl). A band gap of roughly 8 eV is very large, but is close to the experimental value for NaCl. The distance between two atoms is chosen to be $a = 2.82$ Å, which is approximately the nearest-neighbor spacing between a sodium and a chlorine atom in the rocksalt structure. Coulomb potentials will be screened with the usual Slater orbital corrections for Na and Cl [9]. We find numerically that $\tilde{J}_C$ can be represented in Fourier space by multiplying the Fourier transform of the regular Coulomb potential with a Gaussian correction factor, $\exp(-k^2/2a_{\rm S}^2)$, with $a_{\rm S} = 2.78$ Å, leading to $(1/\epsilon_0 a) = 64$ eV. As the Slater screening length $a_{\rm S}$ is only 1.4% less than a, one could simply use a instead of $a_{\rm S}$ in a semi-quantitative calculation.

In principle, we would have to reevaluate the term α for screened interactions. This turns out to be important, as the screening at the R-point in the first BZ [$\mathbf{k} = (\pi/a)(1,1,1)$] becomes extraordinarily strong, due to the exponential dependence of $\tilde{J}_{\rm S}$ on k^2. We therefore replace heuristically the Gaussian dependence with a Lorentzian

$$\begin{aligned}\tilde{J}_{\rm S}(\mathbf{k}) &= \frac{1-\alpha(ak)^2}{(\epsilon_0 \cdot a)\cdot(ak)^2}\cdot \exp\{-(a_{\rm S}k)^2/2\} \\ &\approx \frac{1-\alpha(ak)^2}{(\epsilon_0 \cdot a)\cdot(ak)^2}\cdot\frac{1}{1+(a_{\rm S}k)^2}\end{aligned} \tag{40}$$

so that the second moment of k^2 averaged over the first BZ remains approximately unchanged. In fact, applying this correction factor just to the bare Coulomb potential leads to a screened coupling $J_{\rm MB}(r)$ in real space that was suggested by Müser and Berne to avoid Coulomb singularities in path integral simulations [34]:

$$J_{\rm MB}(r) = \frac{1}{4\pi\epsilon_0}\frac{1}{r}\left(1 - e^{-r/a_{\rm S}}\right), \tag{41}$$

where a_S had been scaled as a function of the Trotter number. The various couplings in real and Fourier space are shown in Fig. 3.

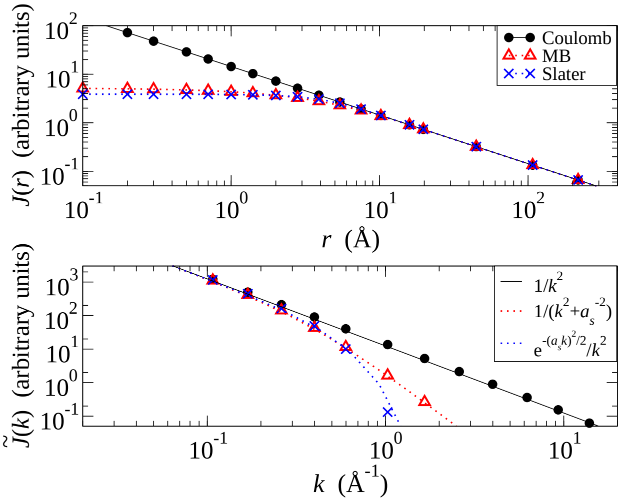

Fig. 3. (Color online) Top: Regular Coulomb coupling (black circles), the screened coupling V_{MB} with the screening length of $a_S = 2.78$ Å(red triangles) and Slater orbital screened Coulomb interactions (blue crosses) with parameters suitable for the interaction between Na and Cl. Lines are drawn to guide the eye. Bottom: Fourier transforms of the above quantities. Lines now represent the given analytical formulas.

In our analysis of the wavelength dependence of the various summands to κ_g, we furthermore revert the continuum approximation to the κ_a-related terms, i.e., we make the following substitution:

$$\kappa_a (ak)^2 \to 2\,\kappa_a \sum_{\alpha=1}^{3} \{1-\cos(ak_\alpha)\}. \tag{42}$$

With these parameters in hand, we investigate how the different summands contribute to the global hardness, which can be done in terms of an an analysis of the "global hardness dispersion". The latter may be loosely associated with the band structure, see Fig. 4. Using the "typical" values for the Coulomb interaction (including screening), we find that there is relatively little wavenumber dependence in the SQE model as long as κ_a is greater than or similar to κ_s. The band gap itself is roughly as large as κ_s. However, if κ_a were much less than κ_s, or even zero as in AACT, negative hardnesses would occur, as discussed earlier. In other words, conduction and valence bands would cross.

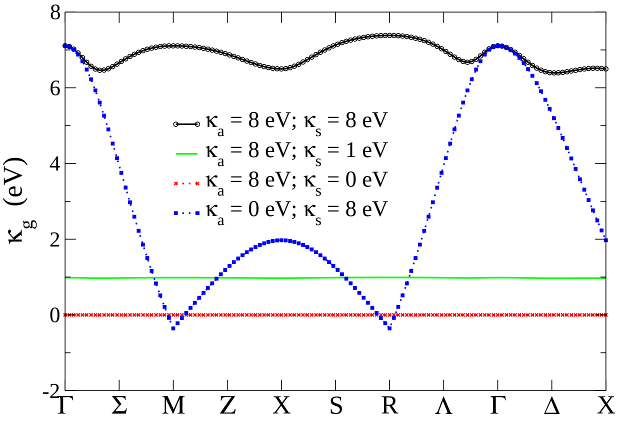

Fig. 4. (Color online) Fourier representation of the global hardness $\kappa_g(\mathbf{k})$ for different choices of the atomic hardness κ_a and the bond hardness κ_s along selected paths in the first Brillouin zone in the simple cubic lattice. The cusps in κ_g at symmetry points are not consequences of the model itself. They are induced by an insufficient accuracy of the Coulomb interactions in a continuum description.

3 Discussion

3.1 Toward force field-based MD simulations of equilibrium redox reactions and zwitterionic molecules

When comparing the electron affinity A of halogens (the highest in the periodic table) to the first ionization energy I of alkali atoms (the lowest in the periodic table), it is not possible to find a pair of stable elements for which an (integer) electron transfer would be energetically favorable ($A > I$) in the diatomic dissociation limit. Therefore, any diatomic molecule in its quantum mechanical ground state dissociates into two neutral atoms. Mimicking this empirical fact is one of the strengths of the split charge concept: κ_s can be made distance dependent so that it diverges in the dissociation limit and no partial charge transfers between the two atoms [17].

As one envisions the simulation of electrolytes or even a battery driving an external electrical load, SQE would be confronted with the problem that any charge exchange between an electron donor and an electron acceptor has so far been described as a polarization of the bond between two atoms but not as a redox reaction. Thus, while atom-based QE methods had the "metallicity" issue, SQE has an "ionicity" problem: Although some SQE atoms may keep some of their "electrons" on the long leash, there are no true ions. Consequently, any current that has flown through an external load in a hypothetical all-atom simulation of a battery would have to be inverted when the circuit breaker is opened again.

The ionicity problem can be overcome by introducing (phenomenologically) *integer* charge transfer between atoms that would not be penalized by a bond stiffness term, e.g., by adding an integer excess charge to one atom in a molecule and removing it from another one. Although integer charge transfer may never be energetically favorable for isolated pairs of atoms, the situation can change when there are more than two atoms present. Equations (16) and (17) show that in the simplest SQE approach, collectivity leads to increased electron affinity as compared to that of isolated atoms and decreased ionization energies. Thus, when considering a system with more than two atoms, integer electron transfer can be energetically favorable and ionic states could be produced even when the two chemical moieties involved in the transfer are separated by distances much exceeding a molecular bond length.

According to the SQE model, integer charge transfer within a molecule would be favored for molecules that have two nearby electronegative atoms within one side chain of a molecule and one or more electropositive atoms at another one. Integer charge exchange over long distances and violation of local charge neutrality would then become beneficial. This corresponds to what is observed in zwitterionic molecules, containing, for example, a negatively charged carboxylate group and a positive ammonium group. A quantitative charge transfer model will certainly necessitate terms reflecting bond order and ionization energies, yet the trends are already captured correctly at the rather generic level pursued in this work.

3.2 Toward force field-based MD simulations of contact electrification, non-equilibrium redox reactions and history-dependent oxidation states

One of the problems of current charge fluctuation models – and also of regular DFT – is that partial changes or charge densities arise as a unique function of the nuclear positions. This is because both DFT and all charge equilibration methods have a unique minimization principle with which charge densities or partial charges are computed. However, in reality, the oxidation state of atoms, molecules, clusters and solids is strongly history dependent, as discussed below. Having means of mimicking this history dependence will be important to describe non-equilibrium redox reactions such as friction-induced contact electrification.

Let us consider two metal blocks with different work functions. Assume that both blocks are in vacuum, initially neutral and separated by a distance that is sufficiently large so that no electrons tunnel between the two metals on relevant experimental time scales. If the two blocks are then brought into close contact, charge is going to flow from the metal with the smaller to that of the larger work function. Once the blocks are separated from one another, the transferred charge is not going to flow back completely. Thus, the partial atomic charges are going to differ between the initial and the final state, although the position of the metals are identical at the beginning and at the end. This would even be true if some daemon ensured that no atom moved throughout the experiment relative to the center of mass of the metal block to which it belongs.

A related thought experiment is the dissociation of an NaCl molecule in the atmosphere of an inert gas. Initially, the chlorine will have an oxidation state of -1 and sodium of +1. If the molecule were to separate adiabatically, two neutral atoms would be formed, but in a fast diabatic dissociation, two charged ions would be the likely result.

The lesson to be learnt from the thought experiments is that partial charges should not be determined based on a unique minimization principle, but that history dependence needs to be included. One should therefore have the ability to describe diabatic and not only adiabatic dynamics, as done, for example in Landau–Zener dynamics [35, 36].

In the SQE model, Landau–Zener type dynamics could be achieved by setting up reasonable rules for the change of oxidation state of atoms. We know that electron transfer between two atoms only occurs (on time scales relevant for MD) when the two atoms are close to one another, i.e., when their outer orbitals overlap, or when they are somehow connected indirectly – as they are in a battery driving an external load, where reduction and oxidation occur spatially separated at anode and catode, respectively. This physical picture can be realized qualitatively with the following algorithm: in an MD simulation, Monte Carlo-like trial moves are introduced in which two chemically bonded atoms are allowed to undergo a redox reaction. These trial moves will require the oxidation state of one atom to increase and that of another atom to reduce. The trial state can be accepted based on the energy difference between old and new oxidation states, for example based on energy minimization, or by using the Metropolis algorithm. When doing such a “redox move” within the SQE formalism, it will be necessary to relax all split charges for the new trial configuration. This can induce a significant computational overhead and lead to many other complications. The most serious complications currently apparent to the author of this paper will be discussed in the following.

3.3 Conservation of energy and momentum

Once a trial redox move has been accepted, the system has changed its state in a discrete – or discontinuous – fashion. Exceptions can occur, for instance when κ_s associated with the two atoms undergoing the redox reaction is zero, because an integer split charge can move back across the bond without any energy penalty. It is known from Marcus theory of redox reactions [37,38] that the energy change associated with an electron transfer reaction is usually small, which, in the context of an accepted SQE redox move, would translate to a small change in energy. Though the change would be small, it is finite in the most general case.

If the redox move has not been subjected to the rules satisfying detailed balance, for example when only those reactions are accepted that minimize the potential energy, one will be interested in ensuring energy conservation. Thus both temperature and energy would not be defined. As many redox reactions are radiation free, it will make sense to change the momenta of the involved atoms in such a way that not only energy but also local momentum is conserved. Otherwise, one risks to destroy hydrodynamic interactions in cases where these are relevant to the dynamics. This is why velocity rescaling would be, once again, a bad idea. Assuming that the momentum transfer is parallel to the unit vector $\hat{r}_{ij}$ pointing from atom j to atom i, the new velocities would have to read

$$m_i \mathbf{v}_{i\,\mathrm{new}} = m_i \mathbf{v}_{i\,\mathrm{old}} + \mathit{\Delta} p \cdot \hat{r}_{ij}, \tag{43}$$

where the momentum transfer $\mathit{\Delta} p$ can be determined from

$$\frac{m_i}{2}\mathbf{v}^2_{i\,\mathrm{new}} + \frac{m_j}{2}\mathbf{v}^2_{j\,\mathrm{new}} = \frac{m_i}{2}\mathbf{v}^2_{i\,\mathrm{old}} + \frac{m_j}{2}\mathbf{v}^2_{j\,\mathrm{old}} + \mathit{\Delta} E_\mathrm{redox}. \tag{44}$$

While there are two solutions for $\mathit{\Delta} p$ in principle, we well choose the one that keeps the velocities unchanged when $\mathit{\Delta} E_\mathrm{redox}$ is zero, i.e.,

$$\mathit{\Delta} p = -p_{ij\,\mathrm{old}} + \sqrt{p^2_{ij\,\mathrm{old}} + 2\mu_{ij}\mathit{\Delta} E_\mathrm{redox}}, \tag{45}$$

where $p_{ij,\mathrm{old}} = \mu_{ij} \cdot \mathbf{v}_{ij\,\mathrm{old}} \cdot \hat{r}_{ij}$ is the relative momentum of atoms i and j in their center-of-mass system, $\mathbf{v}_{ij\mathrm{old}} = \mathbf{v}_{i\mathrm{old}} - \mathbf{v}_{j\mathrm{old}}$ and $\mu_{ij} = (m_i^{-1} + m_j^{-1})^{-1}$ is their reduced mass.

In principle, one could also allow endothermic reactions with the help of Eq. (45), as long as the square root on the right-hand side is real. However, it is not obvious if much would be gained by doing so, in particular because the inverse reaction might happen in the next time step. Lastly, one should be aware that the construction of a symplectic integrator may be difficult or even impossible to derive; even if $\mathit{\Delta} E_\mathrm{redox}$ were zero, there could still be a discontinuity in the forces upon an integer charge transfer.

3.4 Efficiency and linear scaling

Invoking a trial SQE redox move risks to slow down a simulation because of three main reasons. First, a single trial SQE redox move requires, in principle, an up-date of all split charges. This could then turn a local move into an operation that scales at least linearly in N, making a complete MD time step a $> N^2$ operation. Second, a large number of mostly unwanted trial moves might be attempted. Lastly, the system can end up in a frustrated state. These three issues are going to be addressed in the remaining part of this Section.

The problem of having to minimize *all* split charges after a trial redox move for an exact minimization, can be strongly alleviated if one is willing to allow for systematic but controllable errors. They would occur if an update of the split charges were restricted to the vicinity of the redox reaction. Errors would be small because the redox move would signify a perturbation of a local dipole changing the Coulomb energy with distant volume elements only marginally. This is particularly true whenever it is possible to subdivide a system into neutral volume elements. Errors would only be significant if distant atoms were allowed to exchange integer charges. Moreover, even if a redox reaction were accepted, there would be significant backflow, as we have seen in the case study of the NaCl molecule. Going from a '00' to a '$+-$' oxidation state in NaCl only made the charge on each atom change by 0.27 elementary charges. The backflow in "distant" split charges will be much less than that number.

In order to reduce the risk of conducting an abundance of rejected redox moves, each of which necessitating an up-date of many split charges, one will have to restrict attempts to those that have a reasonable probability to be accepted. Moreover, one will also need to avoid "meaningless" redox moves, as they easily occur when κ_s is small or even zero. In the latter case, each redox move will be accepted, because the backflow will exactly compensate the integer charge change in a metallic bond. An oxidation state should usually only change when there is a local excess charge in a dielectric that can hop from one atom to the next, or when a chemical bond is formed or broken. If one can detect either event efficiently, the number of redox trial moves only needs to involve very few of the "active" split charge bonds.

Lastly, consider the frustrated state shown in Fig. 5a. The neutral Cl and the neutral Na atom do not form a chemical bond. A direct charge transfer from the Na to the Cl atom will therefore not be attempted in an SQE treatment. If the redox trial moves would be restricted such that they could only involve two atoms or ions, then the system would remain frustrated, because a doubly ionized sodium is too expensive in energy, see Fig. 5b. The energy barrier is much reduced if one allows charge transfer through an intermediate atom, as shown in Fig. 5c. This would allow for a redox self-exchange reaction with a relatively small (free) energy barrier.

4 Summary and Conclusions

In this work, we study how three different charge equilibration approaches (QE, AACT, and SQE) predict the energy of a system to change when an external excess charge ΔQ is added to it. The intent of this work is neither to justify the models from first principles, such as through valence bond theory, nor to test how well one can reproduce partial charges for given molecular structures. Instead, we are

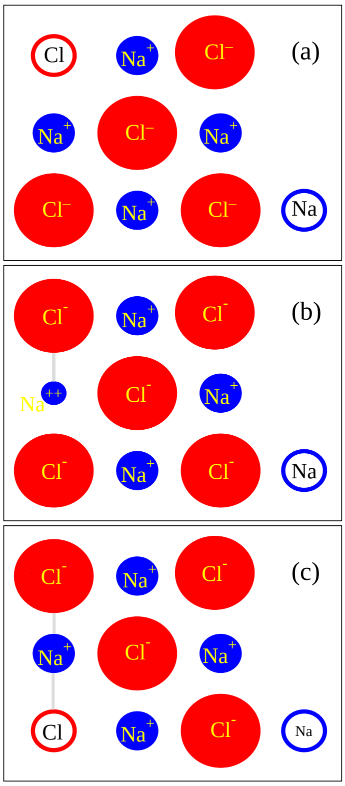

Fig. 5. (Color online) (a) Schematic drawing of a frustrated oxidation state in a NaCl cluster. (b) As long as trial moves only involve two atoms, e.g., the two atoms connected by the grey line, it will be unlikely to change the oxidation state of the two neutral atoms. (c) Allowing for charge exchange between next-nearest neighbors, as those connected by two grey lines, much facilitates charge hopping. The trial configuration in (c) is similar in energy as that in (a). One more such move can then produce a structure in which a Cl with zero oxidation state sits right next to a Na with zero oxidation state.

interested in unravelling *generic* properties, in particular the hardness of molecules and the band gap of solids, and their dependence on system size. This way we can test if predicted *trends* match those observed in real systems, and thereby obtain important clues about if and how modeling charge-transfer reactions can be made possible in simulations based on classical force fields.

It turns out, once more, that QE, AACT, and SQE differ *qualitatively*. The differences regarding their response to excess charges is even more dramatic than those in their dielectric properties (which are summarized in the introduction). When it comes to excess charges, QE is again metallic. The band gap of a QE solid is zero in the thermodynamic limit, and the ionization energy of a molecule does not depend on which atom is donating or receiving an excess charge. The AACT model behaves pathologically in response to excess charges; the molecular hardness is negative and the analogues of valence and conduction bands cross. Although SQE is a hybrid between QE and AACT, it can reproduce the correct dielectric behavior; molecular hardness and band gap are both positive. Moreover, ionization energy and electron affinity depend on what atom in a molecule or solid changed its “oxidation state.” The key quantity for SQE solids is the bond stiffness κ_s. In a previous work, we showed that it is inversely proportional to the dielectric constant in systems like a simple cubic crystal or in rocksalt [20]. Here, we find that the same parameter controls the band gap, at least as long as the charge-equilibration expansion is made around the neutral atom.

The dramatic difference between SQE and AACT might be surprising, because AACT formally emerges as a limiting case of SQE for small atomic hardness. However, this limit is never reached in practice because real atoms have a relatively narrow distribution of atomic hardnesses [29, 39]. As a consequence, κ_s will rarely exceed κ_a. The largest value that we found in our initial SQE work [11] was $\kappa_\mathrm{s} = 5$ eV, describing the chemical hardness of the bond between two tetrahedrally coordinated silicon atoms. This number is slightly larger than the direct band gap of silicon in the diamond structure but still smaller than the atomic hardness of silicon (6.7 eV). Likewise, the large experimental band gap of 8.7 eV in NaCl is less than $\kappa_\mathrm{a}(\mathrm{Na})+\kappa_\mathrm{a}(\mathrm{Cl})$.

It seems as though the SQE model should be suitable for a quantitative calibration. Using a parameterization scheme based on atomic and ionic properties, which are augmented by only one bond stiffness term of $\kappa_\mathrm{s} = 8$ eV that we chose close to the band gap in NaCl, we find that it is possible to produce quite reasonably four important numbers describing the NaCl molecule: the first excitation energy of the neutral molecule, which in the SQE formalism must be associated with $E(\mathrm{Na}^0\mathrm{Cl}^0) - E(\mathrm{Na}^+\mathrm{Cl}^-)$, the first ionization energy $E(\mathrm{Na}^+\mathrm{Cl}^0) - E(\mathrm{Na}^+\mathrm{Cl}^-)$, and the electron affinity $E(\mathrm{Na}^0\mathrm{Cl}^-) - E(\mathrm{Na}^+\mathrm{Cl}^-)$ are all reproduced within one or two eV. Furthermore, the dipole moment is reproduced within 20%. Also metals seem to be described reasonably well in the SQE model in the limit of zero bond hardness. In its simplest variant that does not allow bond-order corrections for the electron affinity, the work function of a metal becomes identical to the electronegativity of the atoms constituting it (since the hardness goes to zero). In reality, the electronegativity is close to 2/3 to 3/4 of the work function of simple metals. Thus, the simple treatment has captured more than 50% of the effect, and moreover reproduced trends correctly.

The results derived in this article may have wide-reaching implications for the force field-based modeling of dynamical processes in various systems, e.g., when redox reactions occur or when zwitterions are present. The calculations show that integer charge transfer, which may not be penalized by a bond stiffness term, can happen in systems consisting of more than two atoms, while simple pairs of atoms always dissociate into neutral atoms in their groundstate. Such integer charge transfer plays an important role in electrolytes and zwitterionic molecules with important consequences for energy materials (batteries) and electrostatics-driven molecular pattern recognition.

Pursuing integer charge transfer in molecular simulation will certainly be a challenging task. In fact, each attempt to move integer charges (be it locally between bonded or also non-locally when conducting wires are present) is likely to necessitate a non-local optimization of all charges. Therefore, it will be challenging, but as outlined in the main text not impossible, to achieve high accuracy and linear scaling of computing time with particle number. Designing rules for SQE pseudo-dynamics that would even roughly mimic real dynamics (in the sense of Ehrenfest) still seems challenging, in particular if one wanted to roughly reproduce Landau–Zener type dynamics. If successful, one would be in a position to simulate processes in which the partial charges and oxidation states of atoms is not only a function of atomic coordinates but may also be history dependent. No force field-based simulation method developed to date can reproduce near-equilibrium contact electrification of an initially neutral metal cluster, which is brought in and out of contact with another metal. In contrast, the proposed modified SQE approach reproduces the dynamics qualitatively. Making the agreement quantitative then merely becomes the question of a good calibration however daunting this task appears to be.

References

1. S. W. Rick and S. J. Stuart. *Rev. Comp. Chem.*, 18:89, 2002.
2. P. E. M. Lopes, B. Roux, and A. D. MacKerell Jr. *Theor. Chem. Acc.*, 124:11, 2009.
3. W. J. Mortier, K. van Genechten, and J. Gasteiger. *J. Am. Chem. Soc.*, 107:829, 1985.
4. U. Dinur. *J. Phys. Chem.*, 97:7894, 1993.
5. In this work, the electronic chemical potential refers to the change of the total energy with respect to charge (expressed in units of the elementary charge e), i.e., $\chi = \mathrm{e} \cdot dV_{\mathrm{pot}}/dQ$. It is often approximated with finite differences from the ionization energy I and the electron affinity A through the equation $\chi = (I + A)/2$. The chemical hardness is defined here as $\kappa = \mathrm{e}^2 \cdot d^2V_{\mathrm{pot}}/dQ^2$. It can be approximated with finite differences through $\kappa = I - A$. Some texts define κ as half the value used here.
6. R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke. *J. Chem. Phys.*, 68:3801, 1978.
7. R. G. Parr and R. G. Pearson. *J. Am. Chem. Soc.*, 105:7512, 1983.
8. P. Itskowitz and M. L. Berkowitz. *J. Phys. Chem. A*, 101:5687, 1997.
9. A. K. Rappé and W. A. Goddard III. *J. Phys. Chem.*, 95:3358, 1991.
10. R. Chelli, P. Procacci, R. Righini, and S. Califano. *J. Chem. Phys.*, 111:8569, 1999.
11. R. A. Nistor, J. G. Polihronov, M. H. Müser, and N. J. Mosey. *J. Chem. Phys.*, 125:094108, 2006.
12. T. Verstraelen, V. Van Speybroeck, and M. Waroquier. *J. Chem. Phys.*, 131:044127, 2009.
13. W. J. Mortier. *Struct. Bonding*, 66:125, 1987.
14. S. M. Valone. *J. Chem. Theo. Comp.*, 7:2253, 2011.
15. T. Verstraelen, P. Bultnick, V. Van Speybroeck, P. W. Ayers, D. Van Neck, and M. Waroquier. *J. Chem. Theory Comput.*, 7:1750, 2011.
16. J. Morales and T. J. Martinez. *J. Phys. Chem. A*, 105:2842, 2001.
17. D. Mathieu. *J. Chem. Phys.*, 127:224103, 2007.
18. P. W. Ayers. *Theo. Chem. Acc.*, 118:371, 2007.
19. G. L. Warren, J. E. Davis, and S. Patel. *J. Chem. Phys.*, 128:144110, 2008.
20. R. A. Nistor and M. H. Müser. *Phys. Rev. B*, 79:104303, 2009.
21. P. T. Mikulski, M. T. Knippenberg, and J. A. Harrison. *J. Chem. Phys.*, 131:241105, 2009.
22. A. Görling and M. Levy. *Phys. Rev. A*, 52:4493, 1995.
23. P. Mori-Sanchez A. J. Cohen and W. T. Yang. *Phys. Rev. B*, 77:115123, 2008.
24. S. W. Rick, S. J. Stuart, and B. J. Berne. *J. Chem. Phys.*, 101:6141, 1994.
25. A. J. Lee and S. W. Rick. *J. Chem. Phys.*, 134:184507, 2011.
26. M. J. L. Sangster, G. Peckham, and D. H. Saunderson. *J. Phys. C: Solid St. Phys.*, 3:1026, 1970.
27. W. T. Yang, C. Lee, and S. K. Ghosh. *J. Chem. Phys.*, 89:5412, 1985.

28. R. G. Pearson. *Acc. Chem. Res.*, 26:250, 1993.
29. J. Robles and L. J. Bartolotti. *J. Am. Chem. Soc.*, 106:3723, 1984.
30. C.-G. Zhan, J. A. Nichols, and D. A. Dixon. *J. Phys. Chem. A*, 107:4184, 2003.
31. R. Mulliken. *J. Chem. Phys.*, 3:573, 1935.
32. J. P. Perdew, R. G. Parr, M. Levu, and Jr. J. L. Balduz. *Phys. Rev. Lett.*, 49:1691, 1982.
33. W. T. Yang, Y. K. Zhang, and P. W. Ayers. *Phys. Rev. Lett.*, 84:5172, 2000.
34. M. H. Müser and B. J. Berne. *J. Chem. Phys.*, 107:571, 1997.
35. L. D. Landau. *Phys. Z.*, 2:46, 1932.
36. C. Zener. *Proc. R. Soc. London A*, 137:696, 1932.
37. R. A. Marcus. *J. Chem. Phys.*, 24:979, 1956.
38. R. A. Marcus. *Annu. Rev. Phys. Chem.*, 15:155, 1964.
39. D. C. Ghosh and N. Islam. *Int. J. Quantum Chem.*, 110:1206, 2010.