A New Approach to Reactive Potentials with Fluctuating Charges: Quadratic Valence-Bond Model

Jorge Morales

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Todd J. Martínez*

Department of Chemistry and The Beckman Institute, University of Illinois, Urbana, Illinois 61801

Received: October 1, 2003; In Final Form: December 22, 2003

Chemical potential equilibration models have proven to be a promising approach for describing charge transfer and polarization in the context of classical force fields. These have generally been justified in an ad hoc manner and are known to behave incorrectly in certain cases, presenting a stumbling block to widespread application. In this paper, we present a new wave function-based derivation of a CPE-like model, shedding some light on the nature of the approximations that are made. The concept of a pairwise hardness arises naturally from this derivation, leading us to suggest a model that employs a pairwise electronegativity. We show that this leads to a CPE-like model that dissociates correctly for a diatomic and furthermore predicts charges in agreement with ab initio methods for a simple diatomic.

Introduction

Since its formulation by Pauling,[1] the concept of electronegativity has formed one of the cornerstones of our qualitative understanding of the chemical bond. There have been attempts to extend the concept for both qualitative and quantitative prediction and a detailed review is available.[2] Certainly these efforts have been influential, for example, the hard−soft acid−base theory of Pearson.[3,4] However, they have also uncovered domains where the concept becomes unwieldy. Because electronegativity is essentially a classical thermodynamic concept and the chemical bond is intrinsically quantum mechanical, this may not be too surprising. Nevertheless, it is fruitful to ask whether simple modifications may significantly extend the domain of applicability.

The electronegativity equalization (EE) postulate of Sanderson[5] forms the basis for several methods to predict atomic partial charges, known by various acronyms as EE or CPE (chemical potential equalization) methods. Early attempts along these lines generally aimed at only qualitative results. Furthermore, these approaches were meant to be applied only at equilibrium molecular configurations and were highly parametrized, requiring assignment of atom types, e.g., sp^2 vs sp^3 carbon atoms.[6,7] Relatively recently, a few workers have developed numerical methods aimed at quantitative accuracy for molecules in arbitrary geometries.[8−12] The goal has been to incorporate fluctuating atomic charges into empirical force fields, thus accounting for polarizability and possibly also true charge transfer. In practice, these methods are most trustworthy when chemically motivated constraints are introduced and the bonding topology does not change. The major problems with extending this type of model to reactive problems are the well-known, but rarely discussed in the literature, deficiencies of incorrect dissociation and excess polarization.[13,14] In particular, application of most of these models to a hetereonuclear diatomic in the gas phase leads to finite, and often nonnegligible, charge transfer at dissociation. In the present work, we explore the origin of these problems with the ultimate goal of developing a model that overcomes them while retaining the elegance and simplicity of CPE methods. A number of fundamental investigations into the electronic structure foundations for electronegativity have been carried out within the context of density functional theory.[15−18] These are quite instructive, but we choose to begin with a wave function picture. Specifically, we begin with a two-state valence bond model and attempt to rigorously derive a CPE method. It is important to note at the outset that because CPE methods dissociate incorrectly, there will of necessity be at least one step that is not physically justified. Nevertheless, we may hope to gain some insight into the character of CPE methods if there are few such steps. Furthermore, this approach may provide some clues as to how the CPE methods can be repaired.

The quest to derive a method of CPE character from first principles leads us to an intermediate model that involves a pairwise hardness. Although this model is ultimately unsatisfying, it does provide the insight needed to formulate a CPE-like model, which is guaranteed to describe dissociation properly for a hetereonuclear diatomic. The results obtained here suggest that it may be fruitful to consider a hierarchy of many-body electronegativities and hardnesses. Even before presenting the results, we can anticipate what this might mean. The atomic electronegativity is correctly interpreted as the propensity of an atom to gain or lose electrons. But in a molecule, one must also consider the proximity to another atom that can accept or donate electrons. In classical thermodynamic terms, one would say that two atoms at infinite separation represent two closed systems and should not be treated as a single open system. At the equilibrium bond length, one might expect them to be well-described as a single open system, and indeed the successes of the electronegativity concept support such a description. A theory that can interpolate between these limits must be able to

---

* Corresponding author. E-mail: tjm@spawn.scs.uiuc.edu.

10.1021/jp0369342 CCC: $27.50

describe “partially open” systems—this can come about naturally through multibody character of electronegativities and/or hardnesses.

Theory

We begin with a quick review of CPE models, following the development of the QEq method by Rappe and Goddard.[8] The charge dependence of the energy of an atom A is expressed in a Taylor expansion as

$$E_A(q_A) = E_A^0 + q_A\frac{\partial E_A}{\partial q_A} + \frac{1}{2}{q_A}^2\frac{\partial^2 E_A}{\partial {q_A}^2} + ... \qquad (1.1)$$

As pointed out by Iczowski and Margrave,[19] using a finite-difference approximation for the derivatives yields

$$\frac{\partial E_A}{\partial q_A} \approx \frac{(IP_A + \mathrm{EA}_A)}{2} = \chi_A^0 = -\mu_A^0$$
$$\frac{1}{2}\frac{\partial^2 E_A}{\partial {q_A}^2} \approx \frac{(\mathrm{IP}_A - \mathrm{EA}_A)}{2} = \eta_A^0 \qquad (1.2)$$

where IP_A and EA_A are the ionization potential and electron affinity of atom *A*. Traditionally, χ_A^0 and η_A^0 are identified as the electronegativity and hardness of the atom A, respectively, and the relevant chemical potential, μ_A^0, is trivially related to the electronegativity, as shown. The energy of a collection of atoms with prescribed partial charges is then expressed as

$$E(q_1,q_2,...q_n) = \sum_i(E_i^0 + q_i\chi_i^0 + {q_i}^2\eta_i^0) + \frac{1}{2}\sum_{i\neq j}q_iq_jJ_{ij}(R_{ij}) \qquad (1.3)$$

where R_{ij} is the distance between atoms *i* and *j*, and $J_{ij}(R_{ij})$ represents the distance dependence of the Coulomb attraction/repulsion between the atoms that in its most naïve form, ignoring the finite extent of the relevant charge distributions, is

$$J_{ij}(R_{ij}) = \frac{1}{R_{ij}} \qquad (1.4)$$

Improved approximations incorporating shielding effects are also possible.[8] Minimizing the energy of this expression with respect to the partial charges q_i is exactly equivalent to Sanderson's electronegativity equalization.[5]

Two difficulties with the resulting expressions can be noted for the case of an isolated atom. First, the QEq energy is a continuous function of the atomic charge. As shown by Parr and co-workers,[20] a derivative discontinuity is physically required at integer atomic charges for an isolated atom. This renders the validity of the Taylor expansion highly doubtful. Second, the energy of the atom should be a monotonically nonincreasing function of the number of electrons. However, this second point depends somewhat on exactly how the atomic charge is defined and might be modified if the added electrons were confined to some finite region around the atom.

We now attempt to derive the QEq model for an isolated diatomic from a wave function approach. As we have noted above, one should not expect this attempt to be completely successful—the QEq model is demonstrably incorrect at infinite separation. Nevertheless, the attempt is instructive and sheds light on the underlying assumptions of CPE models. We begin within a two-state orthogonal valence-bond framework for a neutral diatomic molecule A−B, restricting our attention to two Löwdin-orthogonalized[21] active atomic orbitals, φ_A and φ_B, constructed from nonorthogonal atomic orbitals φ_A^{AO} and φ_B^{AO}, located on atoms A and B as

$$\varphi_A = (\mathbf{S}^{-1/2})_{AA}\varphi_A^{AO} + (\mathbf{S}^{-1/2})_{AB}\varphi_B^{AO} \qquad (1.5)$$

where **S** is the 2 × 2 overlap matrix. In the case of an alkali halide such as NaCl, the active orbitals would be the 3s and $3p_z$ orbitals of Na and Cl. To simplify the derivation for the moment, we assume the more electronegative of the two atoms is B and that the valence bond configuration corresponding to A^-B^+ can be ignored. The total electronic wave function is then given as

$$\psi_{VB} = c_{A^0B^0}\psi_{A^0B^0} + c_{A^+B^-}\psi_{A^+B^-} \qquad (1.6)$$

where

$$\psi_{A^0B^0} = \frac{1}{\sqrt{2}}(|\varphi_A\bar{\varphi}_B\rangle + |\bar{\varphi}_B\varphi_A\rangle)$$
$$\psi_{A^+B^-} = |\varphi_B\bar{\varphi}_B\rangle \qquad (1.7)$$

and multiplication by α (*β*) spin functions is implied by the lack of (presence of) an overbar. Within the framework of Löwdin-orthogonalized orbitals, a natural definition of the partial charge on atom A is $q_A = c_{A^+B^-}{}^2 = 1 - c_{A^0B^0}{}^2$. To make explicit connections to CPE theories, it is convenient to parametrize the wave function in terms of the partial charge rather than the coefficients:

$$\psi^{\pm}(r;q_A) = \sqrt{1 - q_A}\psi_{A^0B^0} \pm \sqrt{q_A}\psi_{A^+B^-} \qquad (1.8)$$

The Hamiltonian matrix in the space of the covalent and ionic configurations is defined as

$$\begin{pmatrix} E_{A^0B^0} & H_{A^0B^0/A^+B^-} \\ H_{A^0B^0/A^+B^-} & E_{A^+B^-} \end{pmatrix} \qquad (1.9)$$

with matrix elements defined using the Löwdin-orthogonalized basis and standard electronic structure theory notation as

$$\begin{aligned} E_{A^0B^0} &= h_{AA}^A + h_{BB}^B + (aa|bb) + (ab|ab) + V_{AA}^B + V_{BB}^A + \frac{Z_A^{\mathrm{eff}}Z_B^{\mathrm{eff}}}{R} \\ &= E_A^0 + E_B^0 + J_{AB} + K_{AB} + V_{AA}^B + V_{BB}^A + \frac{Z_A^{\mathrm{eff}}Z_B^{\mathrm{eff}}}{R} = E_A^0 + E_B^0 + F_{\mathrm{cov}}(R) \\ E_{A^+B^-} &= 2h_{BB}^B + (bb|bb) + 2V_{BB}^A + \frac{Z_A^{\mathrm{eff}}Z_B^{\mathrm{eff}}}{R} \\ &= E_A^0 + E_B^0 + \mathrm{IP}_A - \mathrm{EA}_B + F_B^A(R) \\ H_{A^0B^0/A^+B^-} &= \frac{2}{\sqrt{2}}[h_{AB} + (ab|bb)] \end{aligned} \qquad (1.10)$$

In this equation, we have introduced the operators

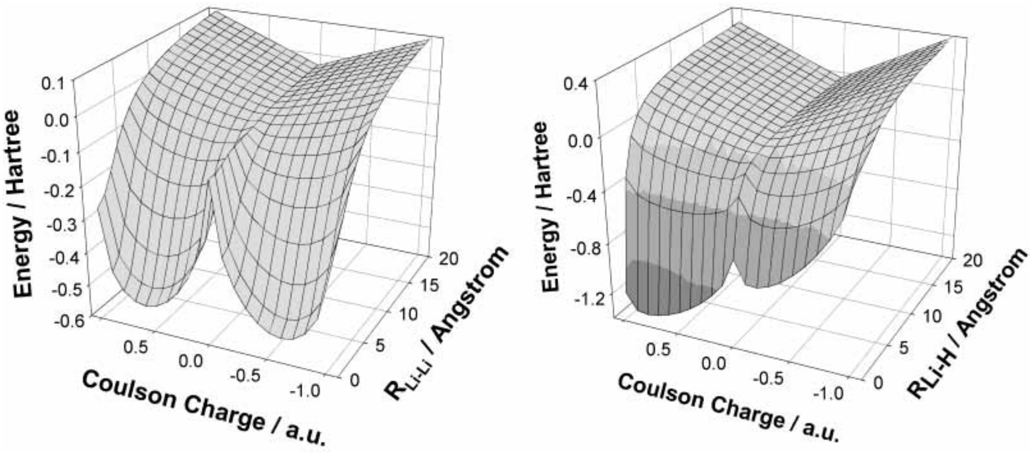

Figure 1. Energy of charge-constrained minimal basis valence bond model for Li_2 (left panel) and LiH (right panel) as a function of bond distance. In both cases, a derivative discontinuity exists at $q = 0$ for all internuclear separations. The Coulson charge is taken positive for Li^+H^- in the LiH case. Notice the different energy scales for the two plots, and the zero of energy is chosen at the separated atoms limit.

$$\hat{h}(i) = \hat{h}^{A}(i) + \hat{V}^{B}(i)$$

$$\hat{h}^{A}(i) = -\frac{1}{2}\nabla^2(i) - \frac{Z_A^{eff}}{r_{iA}}$$

$$\hat{V}^{B}(i) = -\frac{Z_B^{eff}}{r_{iB}} \qquad (1.11)$$

with analogous definitions for $\hat{h}^B$ and $\hat{V}^A$. We introduce effective atomic charges, Z_A^{eff}, for notational convenience, but the development would not be significantly altered if these were replaced by more realistic nonlocal pseudopotentials.[22,23] We have also defined the auxiliary functions

$$F_{cov}(R) = \left(J_{AB} + K_{AB} + V_{AA}^{B} + V_{BB}^{A} + \frac{Z_A^{eff}Z_B^{eff}}{R}\right)$$

$$F_B^A(R) = \left(2V_{BB}^{A} + \frac{Z_A^{eff}Z_B^{eff}}{R}\right) \qquad (1.12)$$

The energy for a given charge q_A is the expectation value of the Hamiltonian:

$$E^{VB\pm}_{A^0B^0/A^+B^-} = (1 - q_A)E_{A^0B^0} + q_A E_{A^+B^-} \pm 2\sqrt{q_A(1 - q_A)}H_{A^0B^0/A^+B^-} \qquad (1.13)$$

If the orbital phases are chosen to make the overlap integral S_{AB} positive, the off-diagonal Hamiltonian matrix element is negative and the lower energy is obtained with the plus sign for the last term. From here on, we assume that such a choice of orbital phases has been made and we restrict our attention to the approximate ground-state energy E^{VB+}. The presence of the square root in eq 1.13 will stymie any attempts to relate this VB expression to CPE theories, and we therefore seek a quadratic approximation. Physical considerations demand that the approximation should vanish at the endpoints, and a suitable choice (from three-point Lagrange interpolation) is therefore

$$2\sqrt{q_A(1 - q_A)} \approx 4(q_A - q_A^{\ 2}) \qquad (1.14)$$

Note that this is not a Taylor expansion about $q_A = 0$, and is exact by construction at $q_A = \{0.0, 0.5, 1.0\}$. Using this approximation, we find the final energy expression (valid only for $0 \le q_A \le 1$) to be

$$E^{VB}_{A^0B^0/A^+B^-} = [E_A^0 + E_B^0 + F_{cov}(R)] + q_A[IP_A - EA_B + F_B^A(R) - F_{cov}(R)] + 4(q_A - q_A^{\ 2})H_{A^0B^0/A^+B^-} \qquad (1.15)$$

A similar expression can be derived by considering the case where the two configurations are $\psi_{A^0B^0}$ and $\psi_{A^-B^+}$, leading to the energy expression (valid only for $0 \le q_B \le 1$):

$$E^{VB}_{A^0B^0/A^-B^+} = [E_A^0 + E_B^0 + F_{cov}(R)] + q_B[IP_B - EA_A + F_A^B(R) - F_{cov}(R)] + 4(q_B - q_B^{\ 2})H_{A^0B^0/A^-B^+} \qquad (1.16)$$

Using the overall charge neutrality, $q_B = -q_A$, these two expressions can be combined in piecewise fashion to describe the domain $-1 \le q_A \le 1$, giving rise to a continuous approximation, but with a derivative discontinuity at $q_A = 0$ for all R. The theory as expressed in eqs 1.15 and 1.16 may be termed charge-constrained quadratic two-state valence bond (CC-QVB2) theory, whereas the analogous theory following from eq 1.13 without Lagrange interpolation will be called charge-constrained two-state valence bond (CC-VB2). In Figure 1, we display the form of the energy in CC-VB2 as a function of both charge and intermolecular bond distance for Li_2 and LiH. In these model calculations, the effective charge on each atom is taken to be 1; i.e., we do not use pseudopotentials. Furthermore, the atomic basis set is composed of two s-type Slater functions with exponents taken from Rappe and Goddard.[8] The derivative discontinuity at $q_A = 0$ is readily apparent. This discontinuity may be numerically troublesome but is a required feature of a correct quantum mechanical model at the dissociation limit.[20] In Figure 2, we compare the CC-QVB2 and CC-VB2 models for Li_2 and LiH at fixed bond distance. The approximation inherent in the Lagrange interpolation does not grossly affect the locations of the observed minima.

At this point, it is natural to take the minimum of the CC-VB2 or CC-QVB2 energy expressions as the optimal charge for a given geometry. This may be an absolute minimum; i.e., the derivative of the energy with respect to charge may be discontinuous at the minimum. However, a more serious problem is that there may be two distinct local minima, and there is no obvious recipe for choosing between them in the zero temperature limit of interest. When the two minima are degenerate, as will always be the case for a homonuclear diatomic like Li_2, the correct solution is to average the optimal charges. This results in no net charge transfer, consistent with symmetry requirements. However, at this point it is not yet clear

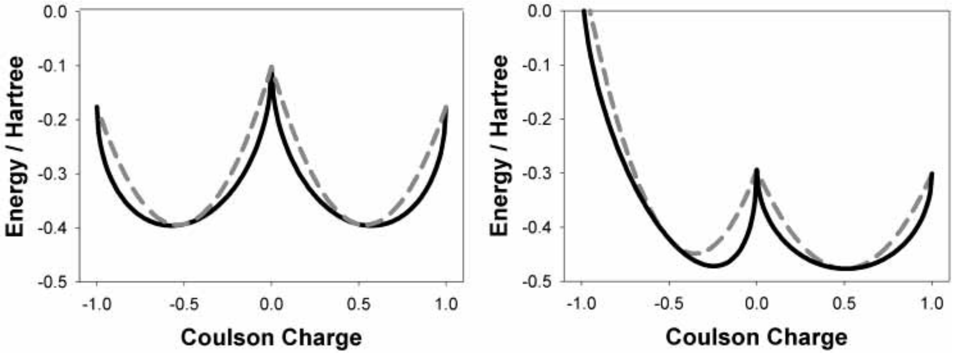

Figure 2. Comparison of CC-VB2 (solid line) and CC-QVB2 (dashed line) models for Li_2 (left panel) and LiH (right panel) at their equilibrium bond distances of 2.67 and 1.60 Å, respectively. The values of the optimal charge for each branch are in reasonable agreement in both cases. The Coulson charge is defined as in Figure 1.

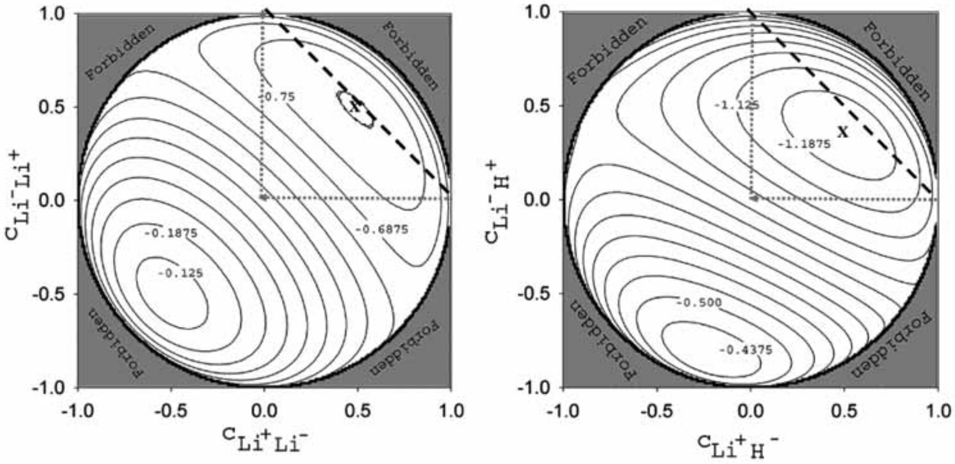

Figure 3. Three-state minimal basis valence bond energy surface for Li_2 (left panel) and LiH (right panel). The remaining coefficient in the wave function, for the covalent configuration, is given by normalization. The regions where the normalization constraint cannot be satisfied with a real coefficient for the covalent configuration are marked "forbidden." Contours are equally spaced, with energies denoted in hartrees, and the zero of energy is arbitrary. In each case, the equilibrium bond distance is used: 2.67 and 1.60 Å for Li_2 and LiH, respectively. The gray dotted arrows indicate the path corresponding to the energy for a given charge used in the CC-VB2 theory. Note that in both cases, there is one minimum and one maximum that are the ground- and excited-state solutions, respectively. The minima are marked with X's. The dashed line indicates an alternative path discussed in the text.

how the solutions should be combined in the general case. To clarify this, it is necessary to consider a more general wave function that simultaneously includes all three valence bond configurations under discussion:

$$\psi^{3-\text{state}} = c_{A^0B^0}\psi_{A^0B^0} + c_{A^-B^+}\psi_{A^-B^+} + c_{A^+B^-}\psi_{A^+B^-} \quad (1.17)$$

We can define the atomic charges derived from this wave function as

$$q_A = {c_{A^+B^-}}^2 - {c_{A^-B^+}}^2$$
$$q_B = {c_{A^-B^+}}^2 - {c_{A^+B^-}}^2 \quad (1.18)$$

In Figure 3, we show contour plots of the resulting energy expression for Li_2 and LiH examples of Figure 2. Note that in the full three-state model, each energy expression has a single minimum and a single maximum, corresponding to the ground- and excited-state solutions, respectively. The CC-VB2 model energy expression corresponds to a restricted one-dimensional path in the two-dimensional space shown by the gray dotted lines. One can easily see from this figure that the sum of the charges associated with the CC-VB2 minima will often be a reasonable approximation to the atomic charges that would be obtained from the three-state model. The presence of two minima in the CC-VB2 and CC-QVB2 models is seen to be a consequence of the particular reduction from two charge transfer variables to a single atomic charge variable. If we instead reduce the three-state model to a two-state model by taking the restricted path given by the dashed line, the resulting energy function would have a single minimum as desired. Furthermore, as one can see from these examples, the minimum along this path is qualitatively similar to the true minimum of the full three-state model. It might be fruitful to develop a model based on this predetermined path, but the resulting expressions are cumbersome and are difficult to relate to electronegativity concepts. We consider two alternative approaches in the following, both of which ensure that there is one unique minimum and therefore a unique atomic charge.

The simplest approach is one of mathematical convenience. By performing a second Lagrange interpolation of the CC-QVB2 energy expression we can guarantee an energy expression with a single minimum and no derivative discontinuity. Applying a three-point Lagrange interpolation to the CC-QVB2 energy expression using the three points $q_A = \{-1, 0, 1\}$ leads to

$$E^{\text{LI-CC-QVB2}}(q_A) = (\chi_A^0 - V_{AA}^B - \chi_B^0 + V_{BB}^A)q_A + (\eta_A^0 + \eta_B^0 - J_{AB} - K_{AB}){q_A}^2 \quad (1.19)$$

where the charge-independent term has been removed for

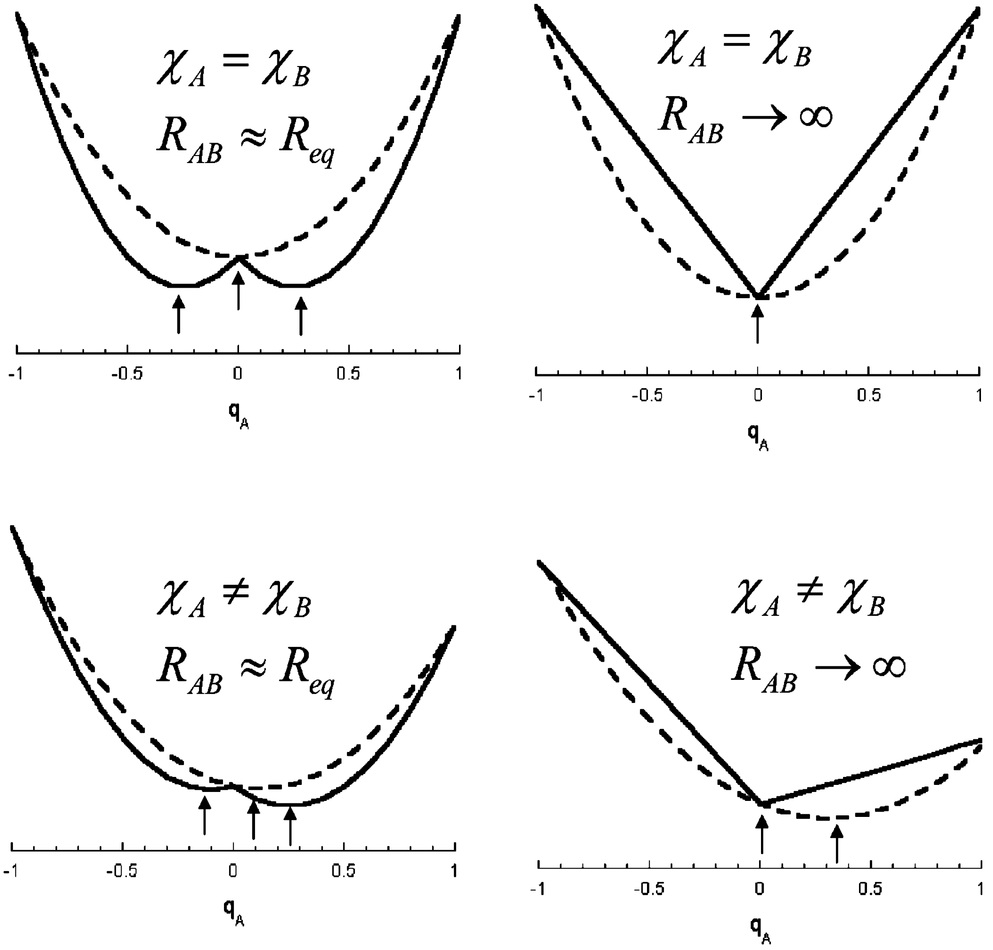

Figure 4. Behavior of the CC-QVB2 (solid) and LI-CC-QVB2 (dashed) energies as a function of charge for four different limiting cases; atoms of equal or dissimilar electronegativty and bond distances near equilibrium or near dissociation. The minima for each of the two energy functions are highlighted by arrows.

simplicity because it has no effect on the predicted optimal charge. This is probably one of the clearest routes from a wave function picture to an electronegativity model. A few key points, absent in the simplest derivations of CPE models, are that the electronegativity is explicitly environment-dependent, the Coulombic interaction is shielded, and an exchange integral appears. It is worthwhile to investigate the origin and behavior of this model in some detail. Figure 4 compares the CC-QVB2 and LI-CC-QVB2 energies as a function of the atomic charge for four limiting cases. The most favorable comparison is obtained in the upper right panel, describing a homonuclear diatomic at the dissociation limit. In this case, the minima of the CC-QVB2 and LI-CC-QVB2 models are identical, although the shapes of the two energy functions are very different. The leftmost panels compare the energy expressions for internuclear separations close to the equilibrium bond distance. In these cases, the CC-QVB2 model often exhibits two minima, whereas the LI-CC-QVB2 model always has a single minimum by construction, as discussed above. For the homonuclear diatomic, where the correct location of the minimum can be deduced by symmetry, the LI-CC-QVB2 model gives the correct solution. The problem, in common with all CPE models, is made clear in the lower right panel, where the LI-CC-QVB2 minimum is at nonzero charge transfer for infinitely separated atoms. The conspicuous absence of environment dependence to the electronegativity in conventional CPE theories can be considered quite puzzling. In Figure 5, we show the form of the environment-dependent correction from eq 1.19 for the specific case of LiH. Although the correction term for each atom is certainly large, it is the difference of the atomic correction terms that enters in eq 1.19. Because the corrections have the same asymptotic form for both

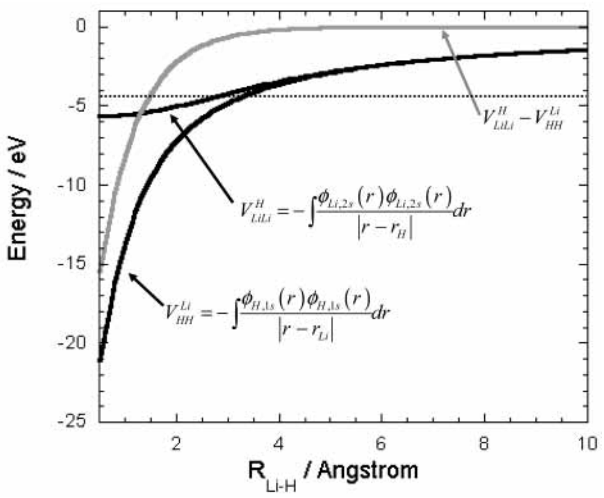

Figure 5. Environment-dependent corrections (black lines) to the electronegativity for Li and H atoms in the LiH molecule as a function of the Li−H separation distance. The gray line shows the difference of the two correction terms (see text) emphasizing that the effect of the corrections can be negligible even when the corrections themselves are sizable. For comparison, the Mulliken electronegativities of Li and H are 3.1 and 7.2 eV, respectively.[2] The difference of these electronegativities is shown as a dotted line.

atoms, their difference vanishes at large separation. The correction takes on a magnitude similar to that of the electronegativity difference ($\chi_{\mathrm{Li}} - \chi_{\mathrm{H}}$) only for very short internuclear separations. Thus, one may speculate that the success of CPE theories in view of their complete neglect of environment-dependence to the electronegativity comes about in part because of a natural cancellation of the correction terms. It is easily seen that the long-range cancellation will be universal, although the domain of internuclear separations where this correction is large will of course be molecule-dependent.

Another way to proceed is to recognize that the two "branches" of the energy expression represented by eqs 1.15 and 1.16 can be interpreted as separate expressions for the energy in terms of charge transfer from A to B and B to A, respectively. Analytic continuation of each branch gives two expressions for the charge-transfer energy, each covering the entire real line:

$$E^{\mathrm{A}\rightarrow\mathrm{B}}(q_{\mathrm{A}\rightarrow\mathrm{B}}) = [E_{\mathrm{A}}^{0} + E_{\mathrm{B}}^{0} + F_{\mathrm{cov}}(R)] + q_{\mathrm{A}\rightarrow\mathrm{B}}[\mathrm{IP}_{\mathrm{A}} - \mathrm{EA}_{\mathrm{B}} + F_{\mathrm{B}}^{\mathrm{A}}(R) - F_{\mathrm{cov}}(R)] + 4(q_{\mathrm{A}\rightarrow\mathrm{B}} - {q_{\mathrm{A}\rightarrow\mathrm{B}}}^{2})H_{\mathrm{A^0B^0/A^+B^-}} \quad (1.20)$$

and

$$E^{\mathrm{B}\rightarrow\mathrm{A}}(q_{\mathrm{B}\rightarrow\mathrm{A}}) = [E_{\mathrm{A}}^{0} + E_{\mathrm{B}}^{0} + F_{\mathrm{cov}}(R)] + q_{\mathrm{B}\rightarrow\mathrm{A}}[\mathrm{IP}_{\mathrm{B}} - \mathrm{EA}_{\mathrm{A}} + F_{\mathrm{A}}^{\mathrm{B}}(R) - F_{\mathrm{cov}}(R)] + 4(q_{\mathrm{B}\rightarrow\mathrm{A}} - {q_{\mathrm{B}\rightarrow\mathrm{A}}}^{2})H_{\mathrm{A^0B^0/A^-B^+}} \quad (1.21)$$

The CC-QVB2 model is trivially recovered if these branches are combined as

$$E^{\mathrm{CC-QVB2}}(q_{\mathrm{A}};q_{\mathrm{B}} = -q_{\mathrm{A}}) = \Theta(q_{\mathrm{A}})E^{\mathrm{A}\rightarrow\mathrm{B}}(q_{\mathrm{A}}) + (1 - \Theta(q_{\mathrm{A}}))E^{\mathrm{B}\rightarrow\mathrm{A}}(q_{\mathrm{B}}) \quad (1.22)$$

where Θ is the Heaviside step function and the restriction of overall charge neutrality is indicated. The presence of the Heaviside step function is not unexpected in view of previous results obtained by analyzing the grand canonical Hartree−Fock model[24−26] in the context of CPE theories, which obtained similar expressions involving Heaviside step functions in the zero temperature limit.[27]

An alternative that is available after the continuation has been performed is to view each of eqs 1.20 and 1.21 as equally valid approximations over the entire domain. In this case, a given charge on atom A can be realized either through electron transfer or hole transfer. In the absence of any clear reason for preferring one description over the other, the final energy expression can be obtained through maximum entropy considerations—the energy of a given charge on atom A is obtained by averaging the two branches corresponding to hole transfer from A to B or electron transfer from B to A. We will call this the maximum-entropy CC-QVB2 model or ME-CC-QVB2, and the resulting energy expression is

$$E^{\mathrm{ME-CC-QVB2}}(q_{\mathrm{A}},R) = E_{\mathrm{A}}^{(0)} + E_{\mathrm{B}}^{(0)} + F_{\mathrm{cov}}(R) + \frac{1}{2}q_{\mathrm{A}}(\mathrm{IP}_{\mathrm{A}} - \mathrm{EA}_{\mathrm{B}} - \mathrm{IP}_{\mathrm{B}} + \mathrm{EA}_{\mathrm{A}} + 2V_{\mathrm{BB}}^{\mathrm{A}} - 2V_{\mathrm{AA}}^{\mathrm{B}}) - 2{q_{\mathrm{A}}}^{2}(H_{\mathrm{A^0B^0/A^-B^+}} + H_{\mathrm{A^0B^0/A^+B^-}}) - 2q_{\mathrm{A}}(H_{\mathrm{A^0B^0/A^-B^+}} - H_{\mathrm{A^0B^0/A^+B^-}}) \quad (1.23)$$

where it is again to be understood that charge neutrality is used to remove q_{B}.

We now introduce approximations for the integrals that are justified by appealing to semiempirical theories. We invoke the Wolfsberg−Helmholtz approximation[28] for the one-electron integrals and the Mulliken−Ruedenberg[29] approximation for Coulomb and exchange integrals, i.e.

$$h_{\mathrm{AB}} = \frac{1}{2}S_{\mathrm{AB}}(h_{\mathrm{AA}}^{\mathrm{A}} + h_{\mathrm{BB}}^{\mathrm{B}} + V_{\mathrm{BB}}^{\mathrm{A}} + V_{\mathrm{AA}}^{\mathrm{B}})$$

$$(ab|bb) = \frac{1}{2}S_{\mathrm{AB}}[(aa|bb) + (bb|bb)] \quad (1.24)$$

where the basis functions in the integrals on the left-hand side are the Löwdin-orthogonalized orbitals and the basis function on the right-hand side are the atomic orbitals. The result is

$$E^{\mathrm{ME-CC-QVB2}} \approx [E_{\mathrm{A}}^{0} + E_{\mathrm{B}}^{0} + F_{\mathrm{cov}}(R)] + \frac{1}{2}q_{\mathrm{A}}\left(\mathrm{IP}_{\mathrm{A}} + \mathrm{EA}_{\mathrm{A}} - \mathrm{IP}_{\mathrm{B}} - \mathrm{EA}_{\mathrm{B}} + 2V_{\mathrm{BB}}^{\mathrm{A}} - 2V_{\mathrm{AA}}^{\mathrm{B}} - \frac{4}{\sqrt{2}}S_{\mathrm{AB}}J_{\mathrm{AA}} + \frac{4}{\sqrt{2}}S_{\mathrm{AB}}J_{\mathrm{BB}}\right) - \frac{1}{2}{q_{\mathrm{A}}}^{2}[J_{\mathrm{AA}} + J_{\mathrm{BB}} + 2(h_{\mathrm{AA}}^{\mathrm{A}} + h_{\mathrm{BB}}^{\mathrm{B}} + V_{\mathrm{AA}}^{\mathrm{B}} + V_{\mathrm{BB}}^{\mathrm{A}}) + 2J_{\mathrm{AB}}]\left(\frac{4}{\sqrt{2}}S_{\mathrm{AB}}\right) \quad (1.25)$$

The last expression can be rearranged for suggestive purposes to

$$E^{\mathrm{ME-CC-QVB2}} = [E_{\mathrm{A}}^{0} + E_{\mathrm{B}}^{0} + F_{\mathrm{cov}}(R)] + \frac{1}{2}q_{\mathrm{A}}\left(\mathrm{IP}_{\mathrm{A}} + \mathrm{EA}_{\mathrm{A}} - 2V_{\mathrm{AA}}^{\mathrm{B}} - \frac{4}{\sqrt{2}}S_{\mathrm{AB}}J_{\mathrm{AA}}\right) - \frac{1}{2}q_{\mathrm{A}}\left(\mathrm{IP}_{\mathrm{B}} + \mathrm{EA}_{\mathrm{B}} - 2V_{\mathrm{BB}}^{\mathrm{A}} - \frac{4}{\sqrt{2}}S_{\mathrm{AB}}J_{\mathrm{BB}}\right) - \frac{1}{2}{q_{\mathrm{A}}}^{2}J_{\mathrm{AA}}\left(\frac{4}{\sqrt{2}}S_{\mathrm{AB}}\right) - \frac{1}{2}{q_{\mathrm{A}}}^{2}J_{\mathrm{BB}}\left(\frac{4}{\sqrt{2}}S_{\mathrm{AB}}\right) - {q_{\mathrm{A}}}^{2}[(h_{\mathrm{AA}} + h_{\mathrm{BB}} + V_{\mathrm{AA}}^{\mathrm{B}} + V_{\mathrm{BB}}^{\mathrm{A}}) + J_{\mathrm{AB}}]\left(\frac{4}{\sqrt{2}}S_{\mathrm{AB}}\right) \quad (1.26)$$

The first term in eq 1.26 is independent of the atomic charges and therefore will have no effect on their optimal values (determined by minimizing the energy). This term can therefore be neglected. We define an environment-dependent electronegativity, which is reminiscent of previous work[30] that has taken $V_{\mathrm{AA}}^{\mathrm{B}}$ as a first-order perturbation term by the approximate Fukui function $f_{\mathrm{A}} \approx {\varphi_{\mathrm{A}}}^{2}$

$$\tilde{\chi}_{\mathrm{A}}^{\mathrm{B}}(R_{\mathrm{AB}}) = \chi_{\mathrm{A}}^{0} - V_{\mathrm{AA}}^{\mathrm{B}} - \frac{2}{\sqrt{2}}S_{\mathrm{AB}}J_{\mathrm{AA}} \quad (1.27)$$

We also define a modified environment-dependent hardness,

$$\tilde{\eta}_{\mathrm{A}}^{\mathrm{B}} = -\left(\frac{1}{2}J_{\mathrm{AA}} + h_{\mathrm{AA}} + V_{\mathrm{AA}}^{\mathrm{B}}\right) = \eta_{\mathrm{A}}^{0} - J_{\mathrm{AA}} - h_{\mathrm{AA}} - V_{\mathrm{AA}}^{\mathrm{B}} \quad (1.28)$$

Unlike the modified electronegativity, the modification to the hardness does not come exclusively through the presence of the other atom. Thus, it is interesting to ask how much different the atomic part of the hardness [first three terms on the right-hand side of eq 1.28] is from the usual hardness, η_{A}^{0}. We compare these values in Table 1, using an s-only Slater basis set with exponents from Rappe and Goddard. Notice that both hardnesses are always positive, as should be expected for a physically reasonable model. Furthermore, the actual values are

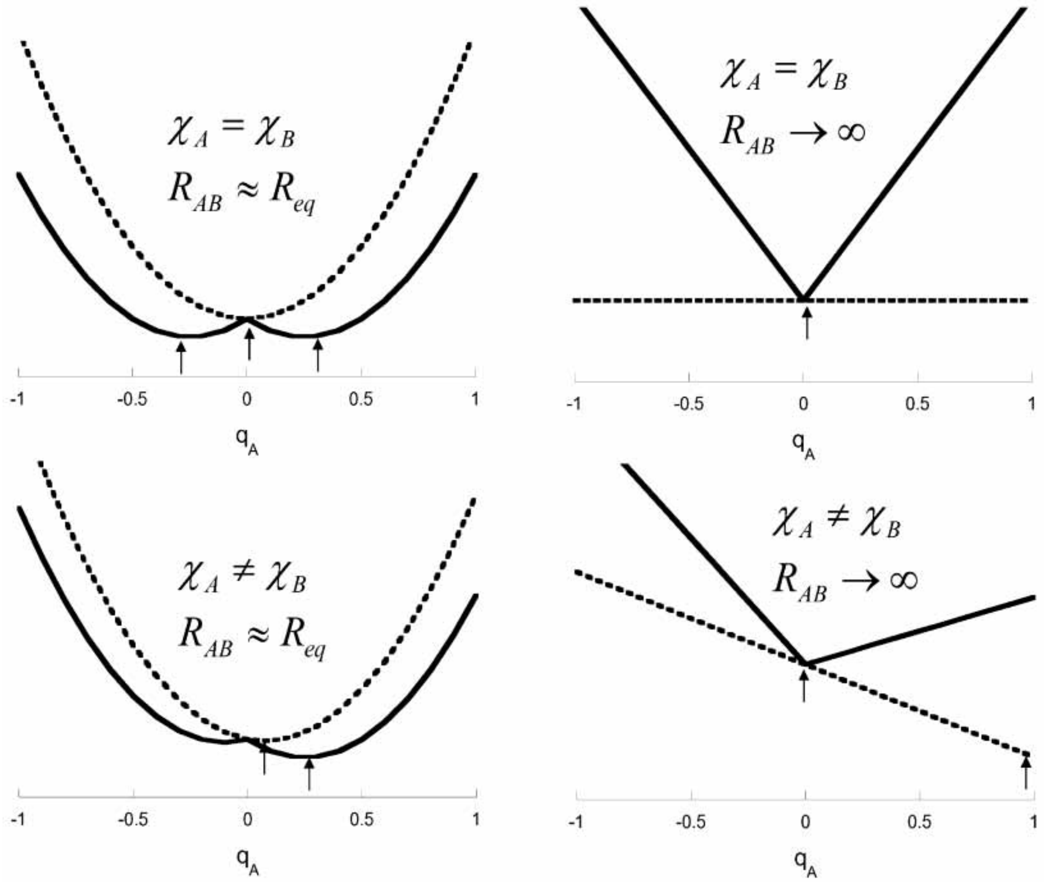

Figure 6. As in Figure 4, but comparing the behavior of the CC-QVB2 (solid) and ME-CC-QVB2 (dashed) energies as a function of charge.

quite similar, with the largest difference occurring for the hydrogen atom.

With the foregoing approximations and simplifications, we may rewrite eq 1.26 as

$$E^{\mathrm{ME-CC-QVB2}} = q_{\mathrm{A}}\tilde{\chi}_{\mathrm{A}}^{B} + q_{\mathrm{B}}\tilde{\chi}_{\mathrm{B}}^{\mathrm{A}} + (\tilde{\eta}_{\mathrm{A}}^{\mathrm{B}}{q_{\mathrm{A}}}^{2} + \tilde{\eta}_{\mathrm{B}}^{\mathrm{A}}{q_{\mathrm{B}}}^{2} + q_{\mathrm{A}}q_{\mathrm{B}}J_{\mathrm{AB}})\left(\frac{4}{\sqrt{2}}S_{\mathrm{AB}}\right) \quad (1.29)$$

This equation is in the form expected from CPE-like theories, provided the last term in parentheses is unity. This occurs when the overlap matrix element is $\sqrt{2}/4$, which is a reasonable average value for an equilibrium A−B bond distance. For comparison, the values of the corresponding matrix elements in H_2, LiF, and NaCl at their equilibrium geometries are 0.7, 0.09, and 0.19. It is completely consistent with the approximation that the overlap matrix element is a constant to also neglect the environment dependence of the electronegativity and hardness (or to absorb these in an averaged way) such that the superscripts on these terms in eq 1.29 may be dropped. Again, we inquire as to the behavior of this new model in various limits, analogously to Figure 4. The results are shown in Figure 6. At finite internuclear separation, the model correctly predicts no charge transfer for a homonuclear diatomic. For hetereonuclear diatomics, finite charge transfer is predicted in general, and this will usually be somewhat less than the prediction of CPE theories. However, the model fails in the limit of infinite internuclear separation for both homonuclear and hetereonuclear diatomics, because the energy function becomes linear in the limit of infinite internuclear separation, whereas the correct result is piecewise linear.

However, we notice a new feature of the ME-CC-QVB2 energy expression that is the effective pairwise nature of the hardness. This is suggestive of an alternative model where the electronegativity becomes a pairwise quantity (as opposed to a strictly atomic property). Thus, transferring the pairwise nature of the hardness to the electronegativity, we write

$$E^{\mathrm{PE-CC-QVB2}} = q_{\mathrm{A}}\chi_{\mathrm{A}}^{0}kS_{\mathrm{AB}} + q_{\mathrm{B}}\chi_{\mathrm{B}}^{0}kS_{\mathrm{BA}} + \eta_{\mathrm{A}}^{0}{q_{\mathrm{A}}}^{2} + \eta_{\mathrm{B}}^{0}{q_{\mathrm{B}}}^{2} + q_{\mathrm{A}}q_{\mathrm{B}}J_{\mathrm{AB}} \quad (1.30)$$

and we christen this the pairwise-electronegativity charge-constrained quadratic valence bond model (PE-CC-QVB2). The constant k is analogous to the factor of $4/\sqrt{2}$ appearing in eq 1.29. One should recognize that the precise value of this factor is somewhat ambiguous even in eq 1.29 because it arises from the scale factors used in the integral approximations that other workers have sometimes modified semiempirically in an attempt to improve the quality of such approximations. It is important to note that we do not claim to have derived eq 1.30—it is only suggested in analogy to eq 1.29. For this reason, we have dropped the superscripts and tilde denoting the modified environment-dependent electronegativity and hardness in eq 1.30. We also suggest that one should take k to be the inverse of the overlap matrix element S_{AB} at or near the equilibrium separation. In this way, the model reduces exactly to a CPE model at equilibrium separations and all the parameters developed for such methods can be carried over directly. A rigorous derivation with well-defined approximations may be possible but is not assured. We continue to pursue this but for now content ourselves to explore the ramifications of the model.

Analogously to Figures 4 and 6, we show in Figure 7 the behavior of the PE-CC-QVB2 energy expression in various

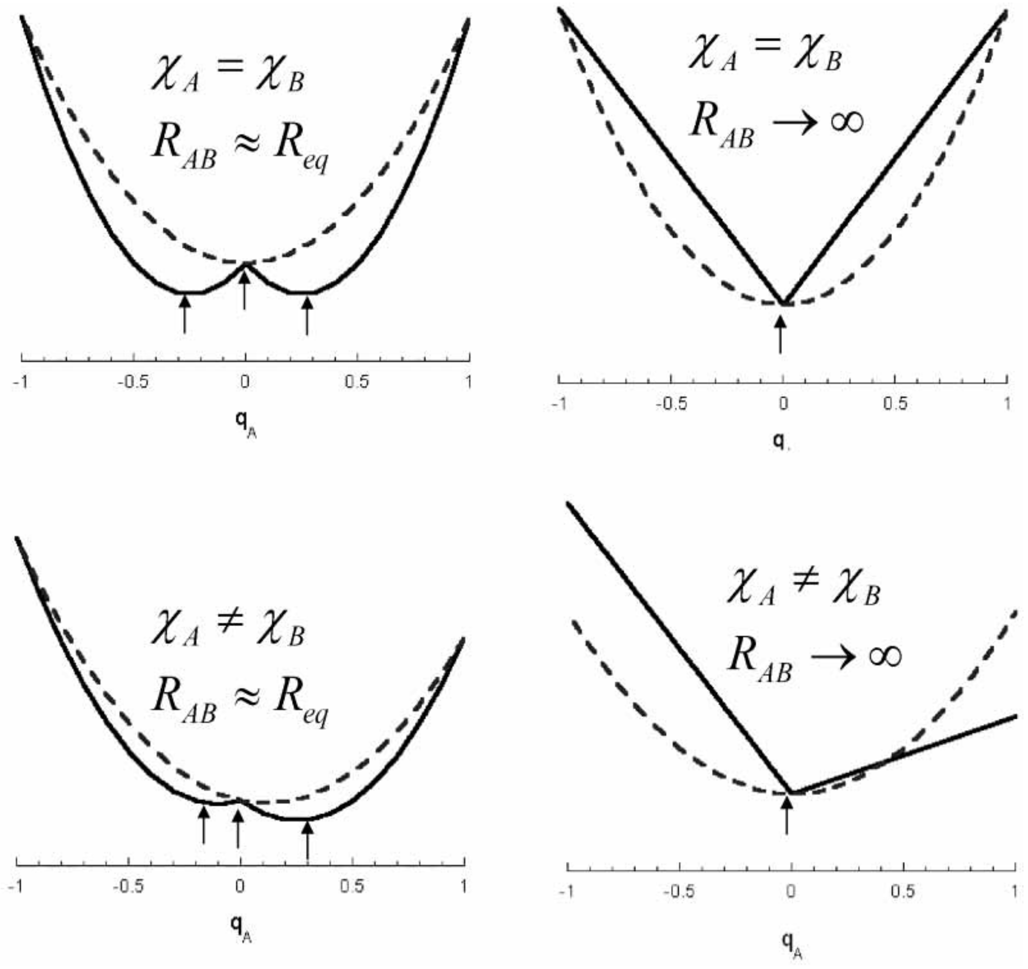

Figure 7. As in Figures 4 and 6, but comparing the CC-QVB2 (solid) and PE-CC-QVB2 (dashed) energies as a function of charge.

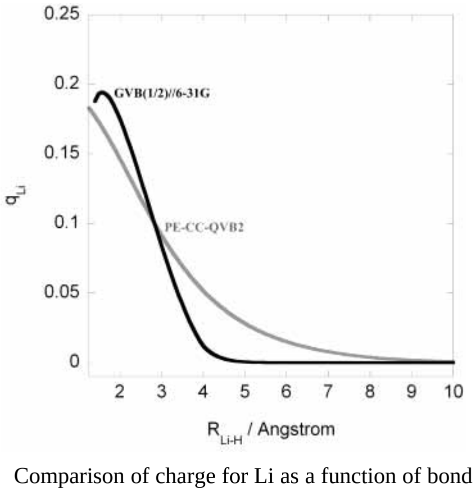

Figure 8. Comparison of charge for Li as a function of bond distance in LiH. The solid black line corresponds to Mulliken charges computed using a GVB(1/2) wave function in a 6-31G basis set, and the gray line is obtained from the parwise electronegativity model described in the text.

limits. In all cases, a single minimum is obtained, and one should especially note the fact that the optimal charge transfer is zero at infinite separation for both the homonuclear and hetereonuclear diatomics, as it should be. As an illustrative example, we apply this model to LiH. The overlap matrix element S_{LiH}, electronegativity, hardness and Coulomb interaction J_{LiH} are all evaluated using the Slater orbital basis proposed by Rappe and Goddard for their QEq model. In Figure 8, we compare the resulting charge for the Li atom from the PE-CC-QVB2 model with that obtained from a GVB(1/2),[31] also known as two-configuration self-consistent field[32] (TCSCF), calculation using Mulliken analysis and the 6-31G basis set. The value for k is 0.33, corresponding to the inverse of S_{LiH} at the equilibrium bond length of 1.6 Å. Considering that we have not fit any parameters for this test, the agreement is quite good.

TABLE 1: Numerical Comparison of Standard Atomic Hardness and Modified Atomic Hardness Implied by Eq 1.28[a]

	$\eta^0_{\mathrm{A}} \equiv (1/2)J_{AA}$	$-(1/2)J_{\mathrm{AA}} - h_{\mathrm{AA}}$
H	9.09	4.31
Li	2.06	2.89
Na	1.53	1.91
F	4.55	4.37
Cl	3.22	2.83

[a] The s-type Slater basis sets of Rappe and Goddard[8] have been used, and the values are given in electronvolts.

Conclusions

We have presented a new derivation of a CPE-like theory (LI-CC-QVB2) for describing charge distributions in molecules. This method differs from conventional methods in the inclusion of explicitly environment-dependent terms. However, we note that these corrections are likely to often cancel and, indeed, rigorously cancel at large separation. Furthermore, the LI-CC-QVB2 theory does not repair the fundamental deficiency of the CPE model, namely finite charge transfer at infinite separation. This led us to an alternative maximum entropy-inspired model

(ME-CC-QVB2) that introduced a pairwise hardness. Although this model also fails in the limit of large separations, it does provide some justification for further explorations of the concept of multibody character in the basic parameters of a CPE theory. The most intriguing result of this paper is the subsequent assertion of a pairwise character to electronegativity.

Although we can provide no rigorous derivation of the core equation for this PE-CC-QVB2 model, we think that it captures the correct chemistry of the molecular charge distribution while retaining the elegance and simplicity of the electronegativity concept. The PE-CC-QVB2 model was tested on a simple case of a dissociating diatomic (LiH) and shown to give good agreement with ab initio derived charges without adjusting any of the parameters from the QEq CPE method. As one can see from Figure 8, the charge transfer is correctly predicted to vanish at inifinite separation in the PE-CC-QVB2 model. This happens because the electronegativities of the constituent atoms vanish at inifinite separation. In this respect, the current model interpolates between conventional CPE theories and a CPE-like theory proposed by Berkowitz,[30] which considered only the hardness and neglected electronegativity. However, Berkowitz' theory was introduced for the specific case of understanding hard−soft acid−base relationships where the electronegativity difference of the reactants is negligible and it was not proposed as a general scheme for computing charge distributions.

One point that should be clear from our work in this paper and its predecessor[27] is that it is unlikely that any quadratic model can escape all difficulties. In the present case, the remaining difficulty is the absence of a derivative discontinuity in the energy at integer charges, i.e., the violation of Janak's theorem.[33] On one hand, this is a blessing numerically. However, it implies that the bond between two atoms has finite polarizability even when the atoms are infinitely separated. This could be inconsequential as long as the polarizability is small. Numerical tests will be required to assess whether it is a problem in practice. Indeed, what needs to be done next is to extend the PE-CC-QVB2 model to arbitrary polyatomics and test its behavior. This work is currently in progress.

Acknowledgment. This work was supported in part by the National Science Foundation (CHE-02-311876 and DMR-99-76550). T.J.M. is grateful to the Packard Foundation and Dreyfus Foundation for a Packard Fellowship and Teacher-Scholar Award. J.A.M. thanks the Robert A. Welch Foundation and Research Corporation for their support. We thank Profs. J. T. Hynes and P. G. Wolynes for helpful discussions.

References and Notes

(1) Pauling, L.; Yost, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **1932**, *18*, 414.
(2) Bergmann, D.; Hinze, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 150.
(3) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(4) Pearson, R. G. *Science* **1966**, *151*, 172.
(5) Sanderson, R. T. *Science* **1951**, *114*, 670.
(6) Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219.
(7) Del Re, G.; Pullman, B.; Yonezawa, T. *Biochim. Biophys. Acta* **1963**, *75*, 153.
(8) Rappe, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 3358.
(9) Rick, S. W.; Stuart, S. J.; Bader, J. S.; Berne, B. J. *J. Mol. Liq.* **1995**, *65*, 31.
(10) Banks, J. L.; Kaminski, G. A.; Zhou, R.; Mainz, D. T.; Berne, B. J.; Friesner, R. A. *J. Chem. Phys.* **1999**, *110*, 741.
(11) York, D. M.; Yang, W. *J. Chem. Phys.* **1996**, *104*, 159.
(12) Stern, H. A.; Kaminski, G. A.; Banks, J. L.; Zhou, R.; Berne, B. J.; Friesner, R. A. *J. Phys. Chem. B* **1999**, *103*, 4730.
(13) Chelli, R.; Procacci, P.; Righini, R.; Califano, S. *J. Chem. Phys.* **1999**, *111*, 8569.
(14) Peslherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. *J. Phys. Chem. A* **2000**, *104*, 4533.
(15) Cioslowski, J.; Stefanov, B. B. *J. Chem. Phys.* **1993**, *99*, 5151.
(16) Cioslowski, J.; Martinov, M. *J. Chem. Phys.* **1994**, *101*, 366.
(17) Itskowitz, P.; Berkowitz, M. *J. Phys. Chem. A* **1997**, *101*, 5687.
(18) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
(19) Iczokowski, R. P.; Margrave, J. L. *J. Chem. Soc.* **1961**, *83*, 3547.
(20) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691.
(21) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365.
(22) Melius, C. F.; Goddard, W. A., III. *Phys. Rev. A* **1974**, *10*, 1528.
(23) Kahn, L. R.; Baybutt, P.; Truhlar, D. G. *J. Chem. Phys.* **1976**, *65*, 3826.
(24) Gyftopoulos, E. P.; Hatsopoulos, G. N. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *60*, 786.
(25) Abdulnur, S. F.; Linderberg, J.; Ohrn, U.; Thulstrup, P. W. *Phys. Rev. A* **1972**, *6*, 889.
(26) Slater, J. C.; Mann, J. B.; Wilson, T. M.; Wood, J. H. *Phys. Rev.* **1969**, *184*, 672.
(27) Morales, J. A.; Martínez, T. J. *J. Phys. Chem. A* **2001**, *105*, 2842.
(28) Wolfsberg, M.; Helmholtz, L. *J. Chem. Phys.* **1952**, *20*, 837.
(29) Ruedenberg, K. *J. Chem. Phys.* **1951**, *19*, 1433.
(30) Berkowitz, M. *J. Am. Chem. Soc.* **1987**, *109*, 4823.
(31) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.
(32) Goddard, J. D.; Handy, N. C.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 1525.
(33) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165.