

# Quantum Mechanical Origins of the Iczkowski–Margrave Model of Chemical Potential

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**ABSTRACT:** Charge flow in materials at the atomistic level is controlled through chemical potential equalization among its constituents. Consequently employing this concept in a simulation requires some model of chemical potential. Current atomistic models of chemical potential, such as the Iczkowski–Margrave (IM) model, are built largely on heuristic arguments and depend linearly on the net charge of each constituent. To gain new insight into the IM model, a many-electron model Hamiltonian is constructed at the atomistic level that is commensurate with the IM model, as opposed to one designed at the one-electron level. For a three-state, two-fragment system, the essential electronegativity and the chemical hardness energies are recovered. However, the model Hamiltonian imparts new charge dependencies not found in the IM model. Decidedly nonlinear, transitional or hopping contributions in those new dependencies are shown to be critical to regulating charge flow. Other modifications to the IM model are illustrated with simple two- and three-fragment systems, involving as many as five states, that act as paradigms for general materials models. Including more than three states in the three-fragment example introduces local bonding refinements to the Mulliken electronegativity and chemical hardness.

## 1. INTRODUCTION

Demands for more refined materials models are driving efforts to ground atomistic levels of those models more fundamentally in the underlying electronic structure. Among the refinements of most intense interest are those pertaining to the chemical potential<sup>1</sup> that determines charge flow among the constituents of a material as they encounter different chemical and mechanical environments.

Numerous variable charge models have been constructed for the purpose of modeling atomic-level chemical potential. The principle model used for this purpose has been that of Iczkowski and Margrave (IM).<sup>2</sup> Specifically, the IM model concerns itself with how the energy of each atom in the material changes with charge fluctuations. Thus, the IM may be viewed as a model of a site energy. The model comes from the simple idea that a site can occupy certain integer charge states (Figure 1),<sup>3–5</sup> most typically the neutral, cation, and anion states. One is naturally inclined to interpolate among those points with a polynomial.<sup>2</sup> With these available states, for an atom A with charge  $q$ , a quadratic polynomial suffices to yield

$$E_A^{\text{IM}}(q) = E_A^{(0)} + \chi_A q + 1/2\eta_A q^2 \quad (1)$$

With  $E_A^{(0)}$  as the energy of the isolated atom, a pleasing interpretation is available by identifying the linear expansion coefficient as the Mulliken electronegativity  $\chi_A$ <sup>4</sup> and the quadratic coefficient as the chemical hardness  $\eta_A$ .<sup>6</sup> Before defining  $\chi_A$  and  $\eta_A$ , first define  $E_A(N_A)$  as the energy of isolated A with  $N_A$  electrons. If A has nuclear charge  $Z_A$ , then  $E(Z_A)$ ,  $E(Z_A - 1)$ , and  $E(Z_A + 1)$  correspond to the energies of the neutral atom, cation, and anion, respectively. The electronegativity is the average of the (first) ionization potential  $I_A$  and electron affinity  $\mathcal{E}_A$ ,  $\chi_A \equiv (I_A + \mathcal{E}_A)/2$ , and while the hardness is the difference  $\eta_A \equiv I_A - \mathcal{E}_A$ . The ionization and electron affinity energies are defined by differences in the energies for isolated atom A with different

numbers of electrons, namely  $I_A \equiv E(Z_A - 1) - E(Z_A)$  and  $\mathcal{E}_A \equiv E(Z_A) - E(Z_A + 1)$ . For future reference, note the finite difference relations  $\chi_A = (E(Z_A - 1) - E(Z_A + 1))/2$  and  $\eta_A = E(Z_A - 1) + E(Z_A + 1) - 2E(Z_A)$ .

The implied chemical potential in the IM model is linear in  $q$ :

$$-\mu_A^{\text{IM}}(q) \equiv dE_A/dq = \chi_A + \eta_A q \quad (2)$$

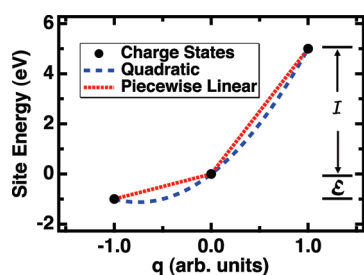
For this reason, some have characterized this model of chemical potential as metallic in nature.<sup>7</sup> Consequently, charge flow is unimpeded when atoms dissociate. This facet of the IM model has led to many variations on the basic theme.<sup>8–22</sup> For the most part, definitions of the coefficients have been made more sophisticated to allow more realistic charge flow over wider ranges of conditions. Nevertheless most of these approaches adhere to a quadratic expansion in  $q$  and retain the essentially metallic nature of the model.

Perdew et al. (hereafter referred to as PPLB) showed that as A dissociates from the rest of the material, the interpolation among integer charge states becomes piecewise linear (Figure 1), instead of a smooth function.<sup>23</sup> The associated model of chemical potential  $\mu_A^{\text{PPLB}}(q)$  is piecewise constant, in marked contrast to the linear IM model. Reconciling these different models has proven difficult. A more fundamental understanding of the origins of the charge dependence of  $E_A(q)$  should prove fruitful. Initial efforts at reconciliation have yielded some progress,<sup>24–26</sup> although they have not yet resulted in a general model of chemical potential.

To this end, a relationship between chemical potential and the stationary principle of density functional theory (DFT) has been proven.<sup>27</sup> That is, suppose that  $E_v[\rho]$  is the energy for an  $N$ - and  $v$ -representable electron density  $\rho$  according to the Hohenberg–Kohn theorem<sup>28</sup> or for an  $N$ -representable density by constrained

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**Figure 1.** Three-state model of site energies underlying the IM model. Both quadratic and piecewise linear interpolations are possible. The resulting models of chemical potential differ dramatically.

search theory,<sup>29</sup> for some fixed external potential  $v$ . Then, for that density to correspond to the ground state of the system, it is necessary that  $\delta E_v / \delta \rho$ , the functional derivative of  $E_v[\rho]$  with respect to  $\rho$ :

$$\mu^{\text{DFT}} \delta E_v / \delta \rho(\mathbf{r}) \quad (3)$$

be a constant, over all points in space  $\mathbf{r}$  (neglecting spin), and where  $\mu^{\text{DFT}}$  is the global chemical potential of the system. The DFT point of view is oriented toward the electronic structure of a molecule or material and provides a value of chemical potential at each point in space. However, the DFT approach to chemical potential is not pursued here.

Rather, we pursue generalizations of the IM definition of chemical potential, a “per atom” quantity,  $\mu_A = \delta E / \delta N_A$ , where  $N_A$  is the number of electrons associated with A. It is generally accepted that  $\mu_A = \mu^{\text{DFT}}$ , although that relationship is not explored here either. We will, however, return to the distinction between finite-difference and differential definitions of electro-negativity and hardness, as they are related to  $\mu_A$ , and to the relationship of  $\mu_A^{\text{IM}}$  to  $\mu_A$ .

Our desire in analyzing the chemical potential is to connect with a certain genre of atomistic models that are founded on eq 2, and where the states of the atoms are the central focus, rather than the states of the electrons defined by eq 3. To attain such a goal, several features of the DFT lines of thinking must be recognized at the outset: (1) Implicit in the vast majority of atomistic materials models is the notion that one can actually define atoms or, more generally, fragments in a material. (2) To make these identifications, the total electron density is often decomposed into fragment quantities, as warranted by DFT<sup>8,30–32</sup> and tight-binding (TB)-based<sup>33</sup> approaches to these models. (3) In both cases, single electrons and their states constitute the basic entity, or finest level of granularity, in the model. Coarser entities, such as atoms and states of atoms, are then reconstituted from these more basic entities. As a result, feature 3 is inconsistent with features 1 and 2.

Consequently, we adopt a different tactic here with an atomistic focus from the outset. A model Hamiltonian is constructed with atoms as the fundamental level of granularity. This model Hamiltonian does share certain commonalities with TB Hamiltonians:<sup>34,35</sup> The total energy decomposes similarly, and descriptions of the basic components will sound familiar. However, there are important differences in actuality. The present development relies on many-electron states of the material. The states of the atoms are derived from the many-electron states, rather than single-electron states. The model Hamiltonian will be defined well-enough that all of its components (described below)

could, in principle, be calculated from wave function-based electron structure methods. Finally, both quadratic-like and piecewise-linear limiting behaviors (compare, for instance, refs 8 and 36–40) may be derived from the present approach.

## 2. FRAGMENT MODEL HAMILTONIAN FORMALISM

The broad framework of the fragment model Hamiltonian requires a combination of three essential elements, these being certain characteristics of many-electron wave functions, Hamiltonian decomposition, and charge-state variables. A fragment is a collection of nuclei and electrons that deemed helpful for the material and problem of interest. Thus, a fragment may be anything from a single atom or a functional group to a unit cell or even a molecule in a molecular fluid or crystal. The charge-state variables pertain to the charge states of the fragments and form the connection back to both the many-electron wave functions and the Hamiltonian decomposition, as described here.

First, for an arbitrary, unnormalized state  $\psi$ , take  $\psi = \sum_i c_i |i\rangle$ , where the  $|i\rangle$  are many-electron, nonadiabatic states, and the  $c_i$  are expansion coefficients. The only required characteristics are that the  $|i\rangle$  be normalized antisymmetric, and, for each fragment, the number of electrons be assigned an integer value. There are a number of definitions of charge that might be used. Here it is only necessary to choose a definition and to apply it consistently in constructing the nonadiabatic states. For convenience at this stage of conceptual development, we also require strong orthogonality, meaning that certain one-particle transition densities between any two nonadiabatic states are neglected. Nothing about orbital basis sets, reference states, density decompositions, or even representations is obligatory. No further specificity in the nonadiabatic states is required at this time.

Now, for any fragment A, define a set of its states by the relations:

$$|A\rangle = \sum_{\zeta} C_{A\zeta} |A^{\zeta}\rangle \quad (4)$$

$$|A^{\zeta}\rangle = \sum_i \delta_{\zeta\zeta_i} c_i |i\rangle / C_{A\zeta} \quad (5)$$

and

$$C_{A\zeta}^2 = \sum_i \delta_{\zeta\zeta_i} c_i^2 \quad (6)$$

The Kronecker  $\delta$  functions select which nonadiabatic contributes to the charge state  $\zeta$  of A. For any set of fragments defining our total system, one has available the identities  $\psi = |A\rangle = |AB\rangle$ , for any fragment A or fragment pair AB. Note that  $|AB\rangle$  is not necessarily a product of fragment wave functions. We note here that the  $c_i^2$  and  $C_{A\zeta}^2$  are equivalent to occupation numbers for the various states. Thus, the value of  $C_{A\zeta}^2$  defines what fraction of the time that A spends in the  $\zeta$  charge state. Finally the fractional number of electrons is  $N_A \equiv \sum_{\zeta} N_{A\zeta} C_{A\zeta}^2$ , where  $N_{A\zeta}$  is the integer number of electrons for the  $\zeta$  charge state.

One familiar prototype for these states is the valence bond states for the neutral hydrogen molecule. The Heitler–London or covalent state places one electron on each atom. For example,  $|\text{cov}\rangle = \phi_L(1)\phi_R(2) + \phi_L(2)\phi_R(1)$ , where  $\phi$  is an arbitrarily chosen orbital and L and R label the left and right atoms of the molecule, respectively, when the bond axis is oriented horizontally and the spin is neglected. The labels “1” and “2” signify the spatial coordinates of electron 1 and 2, respectively. Each of two

ionic states places both electrons on one atom and none on the other. For example,  $|\text{ion}_L\rangle = \phi_L(1)\phi_L(2)$ . Each of these states may be augmented with factors that include explicit correlation. This example can be extended to arbitrary systems and numbers of nonadiabatic states.

Second, recall the well-known fact that any electronic Hamiltonian can be decomposed into a sum of fragment Hamiltonians  $\hat{H}_A$  and purely Coulombic interactions  $\hat{V}_{AB}$  between fragment pairs.<sup>41</sup> Some readers may be familiar with this idea from the field of “atom-in-molecule” (AIM) approaches to atomistic modeling. The principle differences are that fragments do not have to be atoms, and only the concept of Hamiltonian decomposition is adopted from that work. Other concepts associated with the AIM approach, such as orbital representations, are *not* adopted here.

Each fragment Hamiltonian is the same operator as applies to that fragment in isolation, except for one caveat to be explained shortly. In typical fashion,  $\hat{H}_A$  is the sum of kinetic energy, electron–nuclear, and electron–electron operators for its electrons. That is,  $\hat{H}_A = \hat{T}_A + \hat{v}_A + \hat{v}_A^{\text{ee}}$ , where

$$\hat{T}_A = \sum_{j \in \text{electrons of A}} \hat{T}_j$$

$$\hat{v}_A = \sum_{j \in \text{electrons of A}} \sum_{\kappa \in \text{nuclei in A}} \hat{v}_{j\kappa}$$

and

$$\hat{v}_A^{\text{ee}} = 1/2 \sum_{j \in \text{electrons of A}} \sum_{k \in \text{electrons of A} \neq j} \hat{v}_{jk}^{\text{ee}} \quad (7)$$

The Coulombic interactions in  $\hat{V}_{AB}$  are only those that come from electrons on A interacting with the nuclei of B and the electrons of B, plus electrons of B interacting Coulombically with electrons and nuclei of A. These Coulombic terms account for all of the interaction operators not appearing in the fragment Hamiltonians themselves. In the end, this is merely a book-keeping exercise. Thus, from Moffitt,<sup>41</sup> in the general case, the fragment Hamiltonian is simply the total electronic Hamiltonian rewritten as

$$\hat{H}^{(f)} \sum_A \hat{H}_A + \frac{1}{2} \sum_{AB} \hat{V}_{AB} \quad (8)$$

$\sum'$  means a double sum excluding terms with  $B = A$ . To complete the definition of  $\hat{H}^{(f)}$ , and this is the caveat mentioned before, each fragment A must be assigned an integer number of electrons  $N_A$ . Traditionally the assignment  $N_A = Z_A$  has always been adopted. In point of fact, there is no physical requirement for this assignment. In the context of charge-transfer events, a variable distribution of electrons among the fragments seems more appropriate.

As an example of the fragment form of an electronic Hamiltonian, suppose the total system consists of two fragments, A and B, that are atoms, meaning that each fragment has only one nucleus. The total Hamiltonian is  $\hat{H}^{(f)} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB}$ . Assume that the system is neutral, so that  $N = Z_A + Z_B$ , where  $N$  is the total number of electrons. Since there are only two fragments in this example,  $\hat{V}_{AB}$  always contains all of the electrons. It need not be discussed here any further.  $\hat{H}_A(N_A)$  is the Hamiltonian for isolated A with  $N_A$  electrons, and  $\hat{H}_B(N_B)$  is the Hamiltonian for isolated B with  $N_B$  electrons. To maintain neutrality, it is only necessary that  $N_A + N_B = N$ . It is *not* necessary that  $N_A = Z_A$ . Electron indistinguishability falls under the definitions of the

nonadiabatic states. It is perfectly acceptable to arbitrarily assign electrons 1 through  $N_A$  to A and electrons  $N_A + 1$  through  $N$  to B. For instance, for the kinetic energy operator of A,  $\hat{T}_A(N_A) = \sum_{j=1}^{N_A} \hat{T}_j$  and, for B,  $\hat{T}_B(N_B) = \sum_{j=N_A+1}^N \hat{T}_j$ . Similar expressions can be constructed for the other operators in the fragment Hamiltonian. This example begs the question of how many electrons to assign to each fragment.

The crucial and unique notion of the present approach is that each state  $|i\rangle$  defines an electron distribution on  $\hat{H}^{(f)}$ . Symbolically,  $\hat{H}^{(f)}|i\rangle = \hat{H}_i^{(f)}|i\rangle$  with the meaning that  $(\hat{H}_A)_i$  (more explicitly  $\hat{H}_{\zeta_i}^A$ ) is assigned  $N_A^{\zeta_i}$  electrons, the number of electrons appropriate to A for state  $i$ . The contracted representation of the wave function for any fragment A leads to its energy being expressed as

$$\bar{E}_A \sum_{\zeta\zeta'} C_{A\zeta'} C_{A\zeta} \hat{H}_{\zeta\zeta'}^A \quad (9)$$

where  $\hat{H}_{\zeta\zeta'}^A \equiv \langle A^{\zeta'} | \hat{H}_{\zeta\zeta'}^A | A^{\zeta} \rangle$  with  $\hat{H}_{\zeta\zeta'}^A = (\hat{H}_{\zeta'}^A + \hat{H}_{\zeta}^A)/2$ . In density matrix form:

$$\bar{E}_A = \text{tr}(\mathbf{H}_A \mathbf{\Gamma}_A) \quad (10)$$

where  $\text{tr}$  is the matrix trace operator, the density matrix  $\mathbf{\Gamma}_A$  has elements  $C_{A\zeta'} C_{A\zeta}$ <sup>42</sup> and  $\text{tr} \mathbf{\Gamma}_A = 1$  is assumed. Averaging the fragment Hamiltonians in the energy matrix elements ensures that they are hermitian. The fragment–fragment interactions can be brought to an analogous form, namely  $V_{AB} \equiv \text{tr}(\mathbf{V}_{AB} \mathbf{\Gamma}_{AB})$ .

Let us return once more to the diatomic example. In the definition of  $\hat{H}_{\zeta\zeta'}^A$ , the kinetic energy for the fragment Hamiltonian of A becomes

$$\hat{T}_{\zeta\zeta'}^A = 1/2 \left( \sum_{j=1}^{Z_A - \zeta_A} \hat{T}_j + \sum_{j=1}^{Z_A - \zeta'_A} \hat{T}_j \right) \quad (11)$$

It depends explicitly on the values of  $\zeta_A$  and  $\zeta'_A$ . The kinetic energy operators for B are balanced with those of A so that charge neutrality is maintained at all times. As before, analogous expressions may be constructed for the other operators contributing to  $\hat{H}_{\zeta\zeta'}^A$ . The Coulombic operators for the A–B atom interaction may be expressed as

$$\begin{aligned} \hat{V}_{\zeta\zeta'}^{AB} = 1/2 [ & \left( \sum_{j=1}^{Z_A - \zeta} \hat{v}_{jB} + \sum_{j=1}^{Z_A - \zeta'} \hat{v}_{jB} \right) + \left( \sum_{j=Z_A - \zeta + 1}^N \hat{v}_{jA} \right. \\ & + \sum_{j=Z_A - \zeta' + 1}^N \hat{v}_{jA} \left. \right) + \left( \sum_{j=1}^{Z_A - \zeta} \sum_{k=Z_A - \zeta + 1}^N \hat{v}_{jk}^{\text{ee}} \right. \\ & \left. + \sum_{j=1}^{Z_A - \zeta'} \sum_{k=Z_A - \zeta + 1}^N \hat{v}_{jk}^{\text{ee}} \right) ] \quad (12) \end{aligned}$$

Thus,  $V_{AB}$  itself is determined by the matrix of distributions of electrons between A and B, reflected in the  $\hat{V}_{\zeta\zeta'}^{AB}$  operators, even though AB is neutral by assumption. Only the charge state of A is needed, because of the neutrality assumption. In the more general, multifragment case, more complex notation is required. Summing the fragment contributions for a give distribution of electrons recovers the total-system Hamiltonian.

The fragment density matrices defined in eq 10 are of a different ilk<sup>42</sup> than those familiar from contemporary energy density, one-matrix, and two-matrix functionals. One-matrices pertaining to energy functionals, for example, come from integrating the  $N$ -particle density matrix of the system over  $N - 1$  of its electrons. The fragment density matrices are comprised of



coefficients for contracted,  $N$ -electron, nonadiabatic states, organized by the charge states of each fragment. For this reason, there are no problems with representability issues, as arise in *reduced* density matrices.<sup>29</sup>

Combining the various fragment contributions, one obtains a total variational energy:

$$\bar{E} = \sum_A \bar{E}_A + \frac{1}{2} \sum'_{AB} \bar{V}_{AB} \quad (13)$$

Systematic definitions of the fragment contributions, particularly the transitional or hopping elements of the fragment energy matrices, were absent from earlier work.<sup>43</sup> This expression conforms to the ansatz for most empirical and semiempirical potentials in common use. However, it originates from a model Hamiltonian with atomic granularity, rather than from a one-electron Hamiltonian,<sup>16,34,44,45</sup> time-averaged values of fragment charges,<sup>46</sup> or perturbation theory estimates.<sup>47,48</sup> Furthermore, as is common among methods that decompose a many-body Hamiltonian, there are no explicit bond and dihedral angle dependencies. Such dependencies come about implicitly from the properties of the nonadiabatic states and from optimization of  $\bar{E}$ .

Third, the charge  $q$  on A may be defined from the fragment charge occupation numbers,<sup>24,26,49</sup> so that  $q \equiv Z_A - N_A$  in the present notation. If three charge states, 0, +, and −, are accessible to fragment A, then the charge reduces to the expression:

$$q = C_{A^+}^2 - C_{A^-}^2 \quad (14)$$

for  $\text{tr } \Gamma_A = 1$ . That is, the net charge of A is determined by the balance in occupancy of the cation and anion states. The charge range depends only on which nonadiabatic states are admitted to the model.

Note that ordinarily there are more occupation numbers than charges. One method for eliminating the undefined coefficients and defining the energy for a chosen set of fragment charges  $\mathbf{q}$  consists of minimizing the variational energy eq 13 over all possible sets of nonadiabatic coefficients  $\mathbf{c}$  that yield those fragment charges.<sup>43</sup> That is

$$E(\mathbf{q}) \equiv \min_{\mathbf{c} \rightarrow \mathbf{q}} \bar{E}(\mathbf{c}) \quad (15)$$

where  $\mathbf{c} \rightarrow \mathbf{q}$  means any choice of  $\mathbf{c}$  that yields  $\mathbf{q}$ . This definition may be motivated by constrained search density functional theory<sup>29</sup> and viewed as a special form of more general constrained functionals.<sup>50</sup>

Spin variables could be added in a more complete treatment. However, as the IM model does not address spin dependencies in an explicit manner, they are neglected here.

### 3. CHARGE–FLOW REGULATION IN A TWO-STATE, TWO-FRAGMENT MODEL

The development above completes the definition of the model Hamiltonian. The simplest illustration of its use in understanding chemical potential consists of a neutral, two-fragment system, where the fragments are atoms, or more simply a diatomic molecule AB. It is described by two states  $|0\rangle = |A^0B^0\rangle$  and  $|+\rangle = |A^+B^-\rangle$ . Clearly, since there are only two states, the resulting model and the IM model cannot be compatible. Neither electronegativity nor hardness as defined by the finite difference relations associated with eq 2 can

play a role in this simplest application of the fragment model Hamiltonian. On the other hand, new second- and higher-order contributions in the charge dependence play a vital role in regulating charge flow.

To see the divergence between the models, begin with eq 14.<sup>24,25</sup> Since, by choice  $C_{A^-} = 0$ , one arrives at the relations  $C_{A^+} = (q)^{1/2}$  and  $C_{A^0} = (1 - C_{A^+}^2)^{1/2} = (1 - q)^{1/2}$ . The coefficients for B have the same values as for A in this case. The subscript A is dropped from  $q$  since only one charge is needed to define the system. Thus its density matrix, as a function of  $q$ , becomes

$$\Gamma_A = \begin{pmatrix} 1-q & \sqrt{q(1-q)} \\ \sqrt{q(1-q)} & q \end{pmatrix}_A \quad (16)$$

The essential charge dependence of  $E_A(q) = \text{tr}(\mathbf{H}_A \Gamma)$  differs considerably from the IM model. These differences can be brought to light by expanding the fragment energy to obtain

$$E_A(q) = H_{00}^A + (H_{++}^A - H_{00}^A)q + 2H_{0+}^A \sqrt{q(1-q)} \quad (17)$$

where the energy matrix elements are defined in eq 9. The asterisk indicates that these energies come from the system states, rather than the properties of the isolated atoms. A term linear in  $q$  appears with an energy scale determined by a generalized ionization energy  $I_A^* \equiv H_{++}^A - H_{00}^A$ . The associated chemical potential  $\mu_A^*$  may be identified as

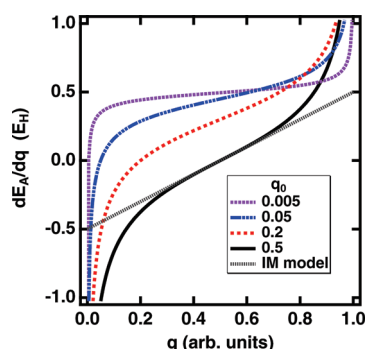
$$\mu_A^*(q) = I_A^* + H_{0+}^A \frac{1-2q}{\sqrt{q(1-q)}} \quad (18)$$

It is evident that a Taylor series representation of  $\mu_A^*(q)$  cannot be centered on either  $q = 0$  or 1. Furthermore, neither the Mulliken electronegativity nor the chemical hardness appear in this model. Instead, first- and higher-order terms appear that have nothing to do with the finite-difference definition of chemical hardness. Whether or not a constant term appears depends on the expansion point used to determine this contribution. At  $q = 1/2$ , no constant appears to combine with the ionization potential. At any other permissible expansion point, a nonzero constant does appear.

Thus, the square-root dependence from the transition matrix elements constitutes a unique facet to the model.<sup>24,25</sup> These dependencies correspond to rigorous density functional<sup>23</sup> and perturbative<sup>51</sup> analyses of nonlinear behavior in the fragment chemical potentials. This model of transitional or hopping contributions to the fragment energies provides a physical basis for the nonlinearities in recently proposed models of chemical potential.<sup>19,20</sup> Hopping contributions constitute departures from thermodynamic models of fractional charge.<sup>40,52</sup>

Transitional contributions do not appear in the IM model and yet constitute the heart of charge flow regulation. To see this, note the following illustration: There is only one charge state for AB so that  $C_{(AB)^0} = 1$ . However, the interaction energy  $V_{(AB)^0}$  depends on  $q$  and may be expressed as a trace over the same density matrix  $\Gamma_{(AB)^0} = \Gamma_A$ . Consequently the total energy simplifies to  $E(q) = \text{tr}(\mathbf{H}_A + \mathbf{H}_B + \mathbf{V}_{AB})\Gamma = \text{tr}\mathbf{H}\Gamma$ . The spectral form of the variational energy<sup>26</sup> is more insightful and can be expressed as

$$E(q) = E_0 + \omega(q)(E_1 - E_0) \quad (19)$$



**Figure 2.** Demonstration of charge flow regulation from differentiating  $E_A(q)$  and compared to the IM model.  $E_A$  is determined from representative values of the  $\mathbf{H}_A$  matrix elements. The ground state charge  $q_0$  is related to the off-diagonal or hopping element of  $\mathbf{H}_A$ .

where  $E_0$  and  $E_1$  are the ground- and excited-state energies derived from these two basis states, and

$$\omega(q) = (\sqrt{(1-q_0)q} - \sqrt{q_0(1-q)})^2 \quad (20)$$

is the occupation number for the excitation. The  $\omega$  depends explicitly on  $q_0$ , the ground-state charge. Because the ground- and excited-state energies are just a special case of the variational energy, each fragment energy and the pair interaction may be recast in a spectral form. That is,  $E_A(q) = E_A^0 + \omega(q)(E_A^1 - E_A^0)$  and  $E_B(q) = E_B^0 + \omega(q)(E_B^1 - E_B^0)$ . A similar expression applies to the pair interaction.

To illustrate how charge transfer is regulated, consider the situation where the bond length  $d$  is large. For this illustration, the spectral forms for each fragment energy are retained. However, the pair interaction is approximated as  $V_{AB}(d;q) \approx V_{AB}^{\text{sr}}(d) - q^2/d$ , where  $V_{AB}^{\text{sr}}$  is a charge-independent short-range contribution and  $-q^2/d$  is a long-range, electrostatic contribution. Similarly, for large  $d$ , all of the atomic contributions,  $E_{A^0}, E_{B^0}, E_1^A - E_0^A \approx \mu_{A^+}^*$ , and  $E_1^B - E_0^B \approx -\mu_{B^-}^*$ , are constant. Define the chemical potential difference  $\mu_{A^+}^* - \mu_{B^-}^* \equiv \Delta\mu$ . These energy gaps come from adiabatic states as opposed to nonadiabatic states, where ionization and electron affinity energies apply. The ground-state charge depends on  $d$ , as denoted by  $q_0(d)$ , and therefore  $\omega = \omega(d;q)$ . Combining these approximations, the illustration becomes

$$E(d;q) \approx E_{A^0} + E_{B^0} + \omega(d;q)\Delta\mu + V_{AB}^{\text{sr}}(d) - q^2/d \quad (21)$$

Setting the partial derivative of  $E(d;q)$  with respect to  $q$  to 0 yields the condition  $2q/d = \omega'(d;q)\Delta\mu$ , where

$$\omega' = 1 - 2q_0 - (1 - 2q)\sqrt{\frac{q_0(1-q_0)}{q(1-q)}} \quad (22)$$

In Figure 2, the point at which the solid, black line crosses one of the nonsolid, colored lines determines the new optimum value of  $q$ . In that Figure,  $\Delta\mu$  is  $0.5 E_H$  and  $2/d = 0.35 E_H$ . As  $q_0$  increases from 0 to 1, more charge is allowed to transfer due to the electrostatic interaction.

The corresponding IM model is

$$E^{\text{IM}}(d;q) \approx E_{A^0} + E_{B^0} + (\chi_A - \chi_B)q + 1/2(\eta_A + \eta_B)q^2 + V_{AB}^{\text{sr}}(d) - q^2/d \quad (23)$$

Its charge equilibration condition may be expressed as  $2q/d = \chi_A - \chi_B + (\eta_A + \eta_B)q$ .  $E^{\text{IM}}$  is shown in Figure 2 for  $\eta_A + \eta_B = 1 E_H$  and  $\chi_A - \chi_B = 0.5 E_H$ . As expected, it transfers the same amount of charge for given atomic properties for all  $d$ . The difference stems from the charge–flow regulation afforded by nonlinear components of  $\omega$ . In turn, those nonlinearities are regulated by the reference charge function  $q_0$ . That function is related to the off-diagonal elements in the fragment energy matrices, that is the propensity for A to transition between charge states.

The chemical potential from eq 18 as derived from  $E_A(q)$  may be compared to the DFT representations.<sup>6,8,37,53</sup> From the present perspective, higher-order contributions originate from the off-diagonal elements of the density matrix. The physics of these transitions pertains to the process of passing from one charge state to another, rather than the energy of the individual charge states per se. These contributions are attributed to environmental effects, an outlook shared by the DFT approach. Significantly, a different, identifiable energy scale is controlling the charge flow, compared to anything available in the IM model. Even more significantly, from the fragment Hamiltonian point of view, the fundamental limitation of the IM model is the basic, nonpolynomial nature of the charge dependence, rather than the spatial dependencies of the energies associated the charges. These contributions enter differential definitions of electronegativity and hardness<sup>6,52–54</sup> but not finite-difference definitions commonly employed by some atomistic models.

#### 4. FRAGMENT HAMILTONIAN INTERPRETATION OF THE IM MODEL

To make more direct contact with the IM model, we examine the charge dependence of the fragment energy for the three-state case of eq 10 for diatomic AB. The state  $|-\rangle = |A^-B^+\rangle$  is readmitted to the set of allowed states.<sup>4,25,43</sup> The fragment density matrix is

$$\Gamma_A(C_+, C_-) = \begin{pmatrix} C_0^2 & C_0 C_+ & C_0 C_- \\ + & C_+^2 & C_+ C_- \\ + & + & C_-^2 \end{pmatrix}_A \quad (24)$$

assuming normalization, while the fragment Hamiltonian, rearranged compared to eq 10, is

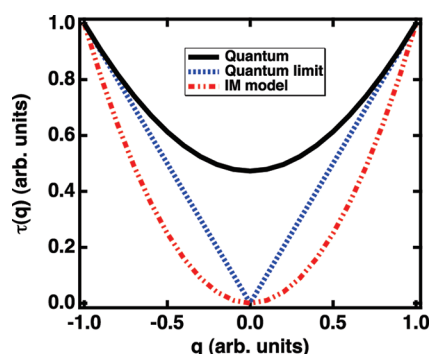
$$\mathbf{H}_A = H_{00} + \begin{pmatrix} 0 & H_{0+} & H_{0-} \\ + & H_{++} - H_{00} & H_{+-} \\ + & + & H_{--} - H_{00} \end{pmatrix}_A \quad (25)$$

This form for  $\mathbf{H}_A$  is used because it more readily highlights the differences with polynomial expansions.<sup>19,20,25</sup> Along the diagonal, both  $I^*$  and a generalized electron affinity  $\mathcal{G}^* \equiv H_{00} - H_{--}$  appear. The generalized electronegativity and hardness have the same relationships to the atomic properties  $I$  and  $\mathcal{G}$  as in eq 1, namely in terms of the energy matrix elements  $\chi^* = (H_{++} - H_{--})/2$  and  $\eta^* = H_{++} + H_{--} - 2H_{00}$ .

To connect the present model to the IM model, let  $\varepsilon_A^0 \equiv H_{00}^A$ . Considering just the diagonal contributions  $\varepsilon_A$  of  $E_A$ , one obtains

$$\varepsilon_A = \varepsilon_A^0 + I_A^* C_{A^+}^2 - \mathcal{G}_A^* C_{A^-}^2 \quad (26)$$

These occupation numbers are not conducive to our analysis, since we want to describe the fragment energies in terms of the net charge as much as possible. As shown previously,<sup>43</sup> these



**Figure 3.** Charge dependence of the hardness term in eq 28 at an OH bond length of 3 Å (solid black) and at the dissociation limit (dashed blue). The IM hardness model (dot-dashed red) is shown for comparison.

occupation numbers can be transformed into functions of  $q$  and an auxiliary variable  $\Lambda$ , such that  $C_{A^+}^2 = (q + \Lambda^2)/(1 + \Lambda^2)$  and  $C_{A^-}^2 = \Lambda^2(1 - q)/(1 + \Lambda^2)$ .<sup>43</sup>  $C_{A^0}^2$  may be determined from normalization. By applying the minimization procedure in eq 15, one can determine  $\Lambda = \Lambda(q)$ .

Instead of  $\Lambda$ , we consider a new variable that complements the net charge. This variable can be identified by rearranging eq 26 according to the definitions of Mulliken electronegativity and chemical hardness. This rearrangement yields

$$\varepsilon_A(C_+, C_-) = \varepsilon_A^0 + \chi_A^*(C_{A^+}^2 - C_{A^-}^2) + \frac{1}{2}\eta_A^*(C_{A^+}^2 + C_{A^-}^2) \quad (27)$$

The new variable is now obvious: It is the total ionic character  $\tau = C_{A^+}^2 + C_{A^-}^2$ . In terms of these variables:

$$\varepsilon_A(q, \tau) = \varepsilon_A^0 + \chi_A^*q + \frac{1}{2}\eta_A^*\tau \quad (28)$$

The net charge dependence associated with the electronegativity is the same as in the IM model. The IM approximation for  $\tau(q)$  is always just  $\tau(q) \approx q^2$ , clearly too simplistic. Alternatively,  $\tau$  can be transformed into a function of  $q$  through eq 15, in the same manner that  $\Lambda$  was made a function of  $q$ , and that is by taking the value of  $\tau$  that minimizes the variational energy for a chosen  $q$ . When this is done, Figure 3 exhibits a charge dependence that contains contributions other than quadratic. Specifically, Figure 3 contrasts the parabolic behavior of the IM model with the present quantum-based arguments, residing in  $\tau(q)$ . The data for the black curve in the Figure were generated from a VB2000 calculation<sup>55,56</sup> for an OH molecule at 3 Å.<sup>43</sup> The dissociation-limit properties are known analytically.

Figure 3 shows how the different fragment energy contributions change as the charge dependence of the site hardness term changes with its environment. When bonds are composed of comparable amounts of covalent and ionic character, the hardness charge dependence is essentially quadratic. The balance of covalent and ionic character changes with bond length though, and  $\tau(q)$  changes shape accordingly. From Figure 3 one can observe that as the bond stretches,  $\tau(q)$  becomes “V-shaped”. Higher-order terms in  $q$  must contribute to the chemical potential simply from the term associated with the chemical hardness. The singularities caused by transforming to charge-dependent variables make it difficult to find uniform polynomial approximations to  $\tau(q)$ . Specifically, the expansion point cannot

in general be at  $q = 0$ . There is no natural alternative expansion, leading to considerable ambiguity in any polynomial representation of the chemical potential.

Presently, no general expression for  $\tau(q)$  is known for finite bond lengths. Based on the limited experience represented in Figure 3, it appears that a reasonable representation of this function might be piecewise polynomials. Then, all but the linear coefficients can be forced to go to 0 as a bond is stretched, so as to match at  $q = 0$ . Assuming that a piecewise representation is indeed appropriate, it is then tempting to hope that substituting a model of  $\tau(q)$  into existing variable-charge models would be sufficient to overcome the deficiencies in the IM chemical potential. This is not so. The transition contributions remain essential in regulating charge flow, just as in the two-state case. A more complete model of chemical potential inherits its properties from these terms as well as those in eq 28.

Finally, we rewrite the three-state fragment density matrix as a function of  $q$  and  $\tau$ . The fragment density matrix of eq 24 becomes

$$\Gamma_A(q, \tau) = \begin{pmatrix} 1 - \tau & \sqrt{(1 - \tau)(\tau + q)/2} & \sqrt{(1 - \tau)(\tau - q)/2} \\ + & (\tau + q)/2 & \sqrt{\tau^2 - q^2}/2 \\ + & + & (\tau - q)/2 \end{pmatrix}_A \quad (29)$$

Viewed in this way, the net charge and ionicity work together in a very specific way to represent the state of A. This is the representation used in the final Section.

## 5. MANY-BODY INTERACTIONS

Because of the fragmentation properties of the many-electron Hamiltonian, any system can be decomposed into a pair of fragments, casting the total system in the form of a pseudodiatom. Obviously the interactions for the pseudopair must differ in a fundamental way from a simple diatomic molecule because of many-body (polyatomic) effects. The question as to how the IM model should be modified for many-body effects is rarely raised. The fragment model Hamiltonian provides one means of addressing this question. The hallmark of a materials environment compared to an isolated diatomic is the increase in coordination. As long as the allowed charge states of the fragments remain the same, the fragment density matrices have the same structure as eq 29. The principle modifications due to many-body effects appear in the fragment energy matrices.

To investigate such many-body effects, we consider two three-fragment systems. In one case, the system is decomposed into an atom by two fragments that consist of a one or more atoms of a different type. The two fragments are assumed to be equivalent to each other. This decomposition corresponds to an impurity view of an atom embedded in a chain. In the other case, the system is decomposed as in the first case, one atom and two fragments. However, the two fragments are bound to each other, and the atom is bound to only one fragment. This decomposition corresponds to an atom of one kind terminating a chain of atoms of another kind. This time the two fragments are not equivalent to each other. One fragment corresponds to the unperturbed bulk chain, while the other fragment corresponds to one or more atoms that are under the influence of the terminating atom.



For the impurity prototype, consider the linear chain A–B–A, where B is the impurity atom in the chain. When it is necessary to distinguish the left- and right-hand fragments, the notation LBR will be used for the chain. Suppose that the unnormalized wave function of ABA involves just five nonadiabatic states,  $|000\rangle$ ,  $|+-0\rangle$ ,  $|+0\rangle$ ,  $|0+-\rangle$ , and  $|0-\rangle$ . Charge transfer between the end fragments is neglected. In keeping with the three-state theme, any fragment can only be singly charged, but they can be either cationic or anionic. The ionic states of B and the neutral states of the end fragments are the most interesting

For B in its many-body environment, it now has two neighbors instead of one. It has contracted states,  $|B^0\rangle = |000\rangle$ ,  $|B^+\rangle = (|+-0\rangle, |0+-\rangle)$ , and  $|B^-\rangle = (|+0\rangle, |0-\rangle)$ . Assuming that the two end fragments are equivalent, the transition energies  $H_{0+}^B$  and  $H_{0-}^B$  have values that are  $\sqrt{2}$  times the value for one resonance. The factor of  $\sqrt{2}$  is the result of normalization considerations.

More generally though, these two expectation values have a dependence on the ratio of coefficients for the charge states of the end fragments. Taking  $H_{0-}^B$  as the primary example, the ratio of interest is  $c_{+-0}/c_{0+-}$ . This ratio may be thought of as being related to the ratio of cation occupancies for the end fragments so that

$$c_{+-0}/c_{0+-} = \sqrt{\frac{n_{L^+}}{n_{R^+}}} \equiv \gamma_{B^-} \quad (30)$$

Recall however that these occupancies are related to the preferred variables  $q$  and  $\tau$ . In terms of these values,  $n_{L^+} = (\tau_L + q_L)/2$  and similarly for the right-hand fragment occupancy. The ratio of interest becomes

$$\gamma_{B^-} = \sqrt{\frac{\tau_L + q_L}{\tau_R + q_R}} \quad (31)$$

Analogous expression, with appropriate notational changes in occupation number ratios, apply to the cation state of B. Specifically,  $\gamma_{B^+} = \sqrt{\frac{\tau_L + q_L}{\tau_R + q_R}}$ .

Moreover, the diagonal energies  $H_{++}^B$  and  $H_{--}^B$  depend on these ratios as well. That is, the state of B and transition among its accessible charge states depends on the state of its environment (defined by the end fragments). Note that the two-state nature of these energies can be exploited. Specifically,

$$H_{++}^B \sim \varepsilon_{B^+} + \omega(\gamma_{B^+}, 1)\Delta\varepsilon_{B^+} \quad (32)$$

and

$$H_{--}^B \sim \varepsilon_{B^-} + \omega(\gamma_{B^-}, 1)\Delta\varepsilon_{B^-} \quad (33)$$

$\Delta\varepsilon_{B^+}$  and  $\Delta\varepsilon_{B^-}$  are characteristic excitations to the charge states of B that would come from the two fragments being forced to be inequivalent. If these excitations are set to zero, then one reverts to a simpler model of the fragment energy. The excitation occupancy is the same function as eq 20 except that it is used in its more seminal form:<sup>26</sup>

$$\omega(\gamma, \gamma_0) = \frac{(\gamma - \gamma_0)^2}{(1 + \gamma^2)(1 + \gamma_0^2)} \quad (34)$$

In the above,  $\gamma_0 = 1$  because the balanced charge distributions correspond to the ground state in the present case, where equivalence of the two A fragments was assumed.

Collectively, from eq 28, the diagonal energy contributions of B fragment  $\varepsilon_B$  may be expressed as

$$\varepsilon_B = \varepsilon_B^0 + \chi_B^* q_B + \frac{1}{2} \eta_B^* \tau_B \quad (35)$$

Now, however, because of the many-body nature of the environment of B, both the effective Mulliken electronegativity and hardness depend on the balances between the individual charge-state occupancies of the end fragments. In detail,  $\chi_B^* = (H_{++}^B(\gamma_{B^+}) - H_{--}^B(\gamma_{B^-}))/2$ , while  $\eta_B^* = H_{++}^B(\gamma_{B^+}) + H_{--}^B(\gamma_{B^-}) - 2H_{00}^B$ . The effective representation of electronegativities derived here suggests a possible path connecting the Mulliken<sup>4</sup> and Phillips<sup>57</sup> scales of electronegativity.

The neutral states of the end fragments are also interesting. For specificity, consider  $|L^0\rangle = (|000\rangle, |0-\rangle, |0+-\rangle)$ , while each of its ionic states involves only one resonance. Recall that, in contrast, B has only one resonance contributing to its neutral state, while the other four contribute to its total ionic character. Thus, in terms of the number of contributions, the neutral state of L<sup>0</sup> is being stabilized by these other two resonances, in comparison to the neutral state of B. Thus, we see that the fragment Hamiltonian view is cognizant of rebalancing ionic character, depending on different bonding environments.

For the chain termination prototype, suppose that A–A–B is described by the same five resonances as in previous example. Now, however, the A fragments are not equivalent, reducing the symmetry in the system. We consider how that asymmetry modifies the effective electronegativities and chemical hardnesses in fragment R (in the LRB notation). Note that the state vector  $|R\rangle$  has the same elements as  $|B\rangle$  in the previous example. Thus the environmental modifications to  $H_{++}^R(\gamma_{R^+})$  and  $H_{--}^R(\gamma_{R^-})$  may be modeled by expressions analogous to eqs 32 and 33, respectively. The difference is that the reference value  $\gamma_0$  for R is no longer unity and does not need to be the same for the cation and anion states of R. These differences stem from the fact that, for example, for the cation state of R,  $\gamma_{R^+} = \sqrt{\frac{\tau_L + q_L}{\tau_B + q_B}}$ . Thus, its reference value will need to take on one that is characteristic of the occupancy ratio of A and B.

Given the environmental dependencies of these fragment energy matrix elements, chemical potential equilibration takes on a new dimension. Equilibration is achieved by optimizing eq 13, subject to the constraint of charge neutrality,  $0 = \sum_A q_A$ . We use  $\mu$  as the Lagrange multiplier associated with enforcing that neutrality. Then, optimization of each charge  $q_\kappa$  leads to  $\mu = -\partial\bar{E}/\partial q_\kappa$ . Expanding  $\partial\bar{E}/\partial q_\kappa$ , one obtains

$$\begin{aligned} \partial\bar{E}/\partial q_\kappa = & \text{tr} \sum_A (H_A \partial\Gamma_A / \partial q_\kappa + \partial H_A / \partial q_\kappa \Gamma_A) \\ & + \sum_{B \neq \kappa} \partial(V_{AB} \Gamma_{AB}) / \partial q_\kappa \end{aligned} \quad (36)$$

In defining  $\partial\bar{E}/\partial q_\kappa$ , one has two choices. In one choice, not only are the other net charges held constant but also the total ionic character variables of each fragment are held constant. Then, a separate optimization process is required to determine those variables. In the other choice, one could assume that the  $\tau$  are functions of their respective  $q$ . The first term is conventional as far as its physical content goes, being directly analogous to the IM model. For either definition of  $\partial\bar{E}/\partial q_\kappa$ , each fragment density matrix  $\Gamma_A$  will depend only on its  $q_A$ . Consequently, the  $\kappa$  term is the sole survivor in the sum over the fragment energies.

The second term,  $\Sigma_A \text{tr} \Gamma_k \partial H_A / \partial q_k$ , is unprecedented. Ordinarily, it is simply set to 0, for lack of a more complete model. Physically  $\partial H_A / \partial q_k$  describes how excitations of A influence the chemical potential of  $k$ , an effect originating from the many-body effects introduced here. These and other effects described in this section are unknown and unavailable in the IM model. The present approach both describes a physical origin to new effects and allows for systematically incorporating them as needed for a particular application. One is then able to select the appropriate level of approximation for a particular problem. Extensions to more complex systems proceed along parallel lines of reasoning.

## 6. CONCLUSION

A new class of model Hamiltonians is constructed where atoms or collections of atoms referred to as fragments, rather than single electrons, are the central entities. Transformation of the wave function expansion variables for the model Hamiltonian provides new models of the charge dependence of a fragment energy and chemical potential. The model smoothly transitions between approximately locally quadratic (in charge) and piecewise linear behaviors. The results stand in contrast to the strictly quadratic behavior of the IM model and help justify other empirical models of charge dependence. Of equal significance, transitions between charge states of the atoms possess distinct energy scales that are wholly absent from the IM model. These transitions bear the highly nonlinear aspects of the chemical potential that regulate charge flow and conform to the analysis of Perdew et al.<sup>23</sup> For simple pairs of fragments, the chemical hardness is shown to be the coefficient for a new variable, the total ionic character. A separate process is required if one wants to make the total ionic character a function of net charge. For systems of multiple fragments, the electronegativity and hardness depend on the balances in charge occupancies of surrounding fragments, as typified by a three-fragment linear chain. The results have broad implications for development of materials models and simulations that have need of dynamical charge variation.

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