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Valence-Bond/Coherent-States Approach to the Charge Equilibration Model I. Valence-Bond Models for Diatomic Molecules

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A valence-bond (VB)/coherent-states (CS) approach to the charge equilibration (CE) model for diatomic molecules is presented in this work (VB part) and its sequel (CS part). By emphasizing theoretical aspects, this approach obtains the classical-electrostatics CE model from a quantum VB model in conjunction with the CS theory. For the VB part, a VB generalized CE (VB/GCE) model, which contains the CE model as a subcase, is derived from a two-electron, three-state VB model via the sequential application of seven approximations. Unlike its CE subcase, the VB/GCE model provides a satisfactory charge-transfer description at dissociation as illustrated with $HF_{(g)}$ and other molecules. Through the previous derivation, CE charges and CE Coulomb interactions are elucidated in terms of VB Mulliken charges and VB atomic interactions, respectively. Modifications in the above derivation can generate a family of related VB/GCE models that includes the aforesaid VB/GCE model. Despite their classical appearance, all of the VB/GCE and CE models involve VB wave functions corresponding to ground and first-excited states. Moreover, all of the VB/GCE and CE energy and charge optimizations are proven to be equivalent to the variational eigenvector equation procedures of the underlying VB models. The quantum-mechanics/classical-electrostatics connection implicit in this work is further elaborated by means of VB CS sets in the sequel. The VB/CS treatment of polyatomic molecules and additional tests of the present approach will be reported in later papers in this series.

1. Introduction

A main endeavor in contemporary electronic structure theory is the simulation of large systems of biochemical, biophysical, and materials science interests. However, even with current computer technology, full quantum-mechanical treatments of such systems remain unfeasible. That difficulty has spurred the development of several methodologies that utilize less-demanding classical-mechanics[1] and/or classical-electrostatics[1,2] descriptions. Depending upon the required level of accuracy, those classical descriptions can be extended to the entire system[1,2] or be restricted to a peripheral region via a quantum/classical (Q/C) partition.[3−7] In that scheme, the system is divided into a central region that encloses quantum phenomena and a background region that is mostly devoid of quantum effects; electrons in the first region are represented explicitly by a wave function or a quantum density; conversely, electrons in the second region (or the entire system if permissible) are represented implicitly by models that circumvent the use of wave functions or quantum densities.

Among several classical methodologies, the charge equilibration (CE)[2] model (also known as fluctuating charge,[8] chemical potential equilibration,[9] or electronegativity equalization[9] model) represents the atoms in a molecule as a set of interacting charges; in that electrostatic picture, the concepts of electronegativity[10] and hardness[11] play prominent roles in defining the molecule energy and in describing charge-transfer reactions. In the subsequent discussion, the CE model will be briefly reviewed within the context of this investigation, but more detailed reviews can be found elsewhere.[12,13] The traditional approach to the CE model involved its derivation from the quantum theory via phenomenological or density-functional-theory (DFT)[12] arguments that have provided different versions of the model. Prominent CE derivations include those by Rappé and Goddard[2] (phenomenological) and by Itskowitz and Berkowitz[14] (DFT-based), inter alia.[12,15] The source of all of those derivations is the seminal analysis by Iczokowsky and Margrave[16] of the variation of the energy of an isolated atom as a function of its charge. From that analysis, it is possible to approximate the energy $E_A^{CE}(Q_A)$ of an atom A as a function of its charge Q_A ($-1 \leq Q_A \leq +1$) with a quadratic interpolating polynomial[17,18] from the energies of three charged species of that atom: E_{A^+}, E_{A^0}, and E_{A^-},

$$\begin{aligned} E_A^{CE} &= E_{A^0} + \frac{(E_{A^+} - E_{A^-})}{2} Q_A + \frac{(E_{A^+} + E_{A^-} - 2E_{A^0})}{2} {Q_A}^2 \\ &= E_{A^0} + \chi_A^0 Q_A + \eta_A^0 {Q_A}^2 \end{aligned} \qquad (1)$$

where χ_A^0 and η_A^0 are the Mulliken electronegativity[10] and the absolute hardness[11] of atom A, respectively. In eq 1, χ_A^0 and η_A^0 satisfy

$$\begin{aligned} \chi_A^0 &= \left(\frac{\partial E_A^{CE}}{\partial Q_A}\right)_{Q_A=0} = -\mu_A^0 = \frac{1}{2}(IP_A + EA_A); \\ \eta_A^0 &= \frac{1}{2}\left(\frac{\partial^2 E_A^{CE}}{\partial {Q_A}^2}\right)_{Q_A=0} = \frac{1}{2}(IP_A - EA_A) \end{aligned} \qquad (2)$$

where $IP_A = E_{A^+} - E_{A^0}$ and $EA_A = E_{A^0} - E_{A^-}$ are the ionization potential and electron affinity of atom A, respectively. In eq 2, the Mulliken electronegativity, χ_A^0, is identified as the negative of the chemical potential of the uncharged atom, μ_A^0, since in general $\mu_A = -\partial E_A/\partial q_A$.[12,19] The CE energy $E_{Molecule}^{CE}$ for a molecular system is the extension of the single-atom CE energy E_A^{CE} to a set of atoms forming a molecule. For a system of N_{Atom} atoms having atomic charges: $\{Q_A, Q_B, ... Q_{N_{Atom}}\}$ and carrying atomic spatial orbitals: $\{\phi_A, \phi_B, ... \phi_{N_{Atom}}\}$, the Itskowitz−Berkowitz CE energy $E_{Molecule}^{CE}$ is as follows:[14]

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$$E^{\mathrm{CE}}_{\mathrm{Molecule}}(Q_{\mathrm{A}}, Q_{\mathrm{B}}, ...\, Q_{N_{\mathrm{Atom}}}) = \sum_{\mathrm{A}}^{N_{\mathrm{Atom}}} (E_{\mathrm{A}^0} + \chi^*_{\mathrm{A}} Q_{\mathrm{A}} + \eta^0_{\mathrm{A}} Q_{\mathrm{A}}{}^2) + \sum_{\mathrm{A<B}}^{N_{\mathrm{Atom}}} \mathrm{J}^{\mathrm{CE}}_{\mathrm{AB}} Q_{\mathrm{A}} Q_{\mathrm{B}} \quad (3)$$

where $J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}}) = J_{\mathrm{AB}}(R_{\mathrm{AB}}) = (\phi_{\mathrm{A}}\phi_{\mathrm{A}}|\phi_{\mathrm{B}}\phi_{\mathrm{B}})$ is the Coulomb integral of the atomic orbitals on atoms A and B at separation R_{AB}, and χ^*_{A} is the environment-perturbed Mulliken electronegativity[14] of atom A

$$\chi^*_{\mathrm{A}} = \chi^0_{\mathrm{A}} - \sum_{\mathrm{B}\neq\mathrm{A}}^{N_{\mathrm{Atoms}}} \int \left[\hat{V}_{\mathrm{B}}(\mathbf{r}_1) + \int \frac{\rho_{\mathrm{B}}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\right] f_A(\mathbf{r}_1) d\mathbf{r_1} \quad (4)$$

where $f_{\mathrm{A}}(\mathbf{r}_1)$ is the Fukui function[20] of that atom ($f_{\mathrm{A}}(\mathbf{r}_1) \approx \rho^{\mathrm{HOMO}}_{\mathrm{A}}(\mathbf{r}_1) = |\phi_{\mathrm{A}}(\mathbf{r}_1)|^2$ [12]), and $\hat{V}_{\mathrm{B}}(\mathbf{r_1})$ and $\rho_{\mathrm{B}}(\mathbf{r_2})$ are the nuclear potentials and charge densities of all the atoms B $\neq$ A. Equation 3 can be interpreted in electrostatic terms: its first sum combines the CE energies $E^{\mathrm{CE}}_{\mathrm{A}}(Q_{\mathrm{A}})$ of the individual atoms, now with an environment-perturbed electronegativity, χ^*_{A}, and its second sum contains the Coulomb interactions $J^{\mathrm{CE}}_{\mathrm{AB}} Q_{\mathrm{A}} Q_{\mathrm{B}}$ between all pairs of atomic charges Q_{A} and Q_{B}. In the latter, $J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}})$ acts as a modulating factor to satisfy boundary conditions. If atoms A and B are well separated ($R_{\mathrm{AB}} \to \infty$) then $J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}}) \to 1/R_{\mathrm{AB}}$ and the Coulomb interaction becomes the ordinary Coulomb law. Conversely, if those atoms are close then $J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}}) \neq 1/R_{\mathrm{AB}}$ and provides a shielded Coulomb law that avoids an unphysical singularity at $R_{\mathrm{AB}} = 0$ because $J^{\mathrm{CE}}_{\mathrm{AB}}$ is finite therein. Notice that the Rappé–Goddard[2] CE energy expression can be obtained from eq 3 if the electronegativity perturbation terms are neglected ($\chi^*_{\mathrm{A}} \approx \chi^0_{\mathrm{A}}$).

The calculation of the optimal CE energy and charges is achieved by applying the Sanderson Principle of Electronegativity Equalization (SPEE)[9] to the CE model; that application explains the term "CE" as seen shortly. According to the SPEE, if atoms combine to make a molecule while retaining their own identities, then their individual CE chemical potentials $\mu_{\mathrm{A}} = -\partial E^{\mathrm{CE}}_{\mathrm{Molecule}}/\partial Q_{\mathrm{A}}$ must equalize to attain chemical equilibrium; that condition leads to $N_{\mathrm{Atom}} - 1$ equilibrium conditions: $\mu_{\mathrm{A}} = \mu_{\mathrm{B}} = ... = \mu_{N_{\mathrm{Atom}}}$ that along with the conservation of the total charge, $Q_{\mathrm{Total}} = \sum_{\mathrm{A}}{}^{N_{\mathrm{Atom}}} Q_{\mathrm{A}}$, render a system of N_{Atom} linear equations for the N_{Atom} optimal charges: $\bar{Q}_{\mathrm{A}}$, $\bar{Q}_{\mathrm{B}}$,... $\bar{Q}_{N_{\mathrm{Atom}}}$[2]. In the case of neutral diatomic molecules AB, the CE energy $E^{\mathrm{CE}}_{\mathrm{AB}}$ from eq 3 can be rewritten in an abridged form that incorporates the conservation of the total charge: $Q_{\mathrm{Total}} = Q_{\mathrm{A}} + Q_{\mathrm{B}} = 0$ via $Q_{\mathrm{A}} = -Q_{\mathrm{B}}$

$$E^{\mathrm{CE}}_{\mathrm{AB}}(Q_{\mathrm{A}}) = A^{\mathrm{CE}} + B^{\mathrm{CE}} Q_{\mathrm{A}} + C^{\mathrm{CE}} Q_{\mathrm{A}}{}^2 \quad (5)$$

where

$$A^{\mathrm{CE}} = E_{\mathrm{A}^0} + E_{\mathrm{B}^0};\ B^{\mathrm{CE}} = \chi^*_{\mathrm{A}} - \chi^*_{\mathrm{B}};\ C^{\mathrm{CE}} = \eta^0_{\mathrm{A}} + \eta^0_{\mathrm{B}} - J^{\mathrm{CE}}_{\mathrm{AB}} \quad (6)$$

In that case, it is easy to prove that the SPEE optimal charge $\bar{Q}_{\mathrm{A}} = -\bar{Q}_{\mathrm{B}}$ corresponds to the condition $dE^{\mathrm{CE}}_{\mathrm{AB}}(\bar{Q}_{\mathrm{A}})/dQ_{\mathrm{A}} = 0$ so that

$$\bar{Q}_{\mathrm{A}} = -\bar{Q}_{\mathrm{B}} = -\frac{B^{\mathrm{CE}}}{2C^{\mathrm{CE}}} = \frac{\chi^*_{\mathrm{B}} - \chi^*_{\mathrm{A}}}{2[\eta^0_{\mathrm{A}} + \eta^0_{\mathrm{B}} - J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}})]} \quad (7)$$

Equation 7 portrays the intramolecular charge transfer leading to the optimal charges as a reaction driven by the electronegativity difference, $\chi^*_{\mathrm{B}} - \chi^*_{\mathrm{A}}$, in accordance with the intuitive notion of electronegativity.

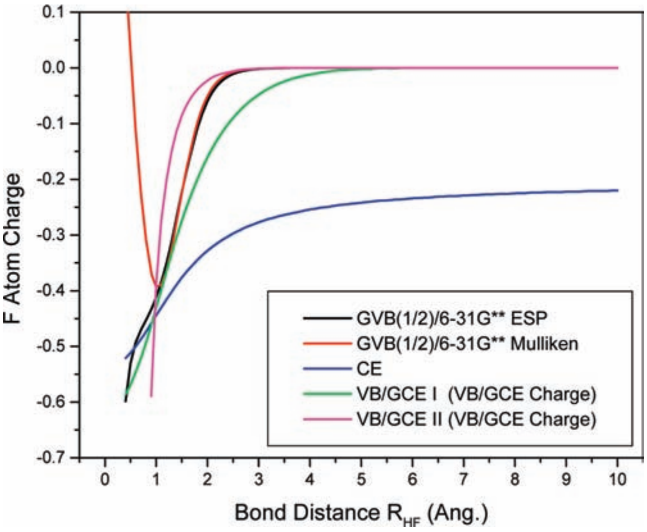

Figure 1. F atom charge in $\mathrm{HF}_{(g)}$ as a function of the bond distance (R_{HF}) from two quantum methods: electrostatic potential (ESP) fitting[23−25] and Mulliken charges from generalized valence-bond (1/2)[36] [GVB(1/2)]/6-31G** calculations, and from three classical methods: Goddard−Rappé CE[2], eq 7, VB/GCE I and II, eq 36, charges.

Furnished with adequate parametrizations, the CE model can satisfactorily predict atomic charges in large molecules near their equilibrium geometries at low computational cost.[2,14] However, despite those advantages, the CE model exhibits significant deficiencies that have hindered its further development and widespread application.[13] While a complete account of all those deficiencies is given elsewhere,[13] this investigation will only address the most primary problems in the CE model. Some of the CE deficiencies manifest as theoretical uncertainties in the CE expressions. For instance, a characterization of the CE atomic charges in terms of standard theoretical definitions of atomic charges (e.g., via Mulliken population analysis,[21,22] electrostatic potential fitting,[23−25] etc.) is missing; similarly, the adoption of $J^{\mathrm{CE}}_{\mathrm{AB}}(R_{\mathrm{AB}})$ as a shielding factor in some CE derivations[2] is obviously ad-hoc because it has not been rigorously derived from the interatomic interactions. However, a more serious deficiency involves the application of the CE equations to bond-breaking processes. It is well-known that the gas-phase dissociation of a ground-state diatomic molecule $\mathrm{AB}_{(g)}$ always yields its uncharged atoms: $\mathrm{A}^0_{(g)} + \mathrm{B}^0_{(g)}$ rather than its ions: $\mathrm{A}^+_{(g)} + \mathrm{B}^-_{(g)}$, $\mathrm{A}^-_{(g)} + \mathrm{B}^+_{(g)}$, etc., because in practice $\mathrm{IP}_{\mathrm{A/B}} - \mathrm{EA}_{\mathrm{B/A}} > 0$. However, eq 7 predicts for $\bar{Q}_A$ ($= -\bar{Q}_B$) at dissociation,

$$\lim_{R_{\mathrm{AB}}\to\infty} \bar{Q}_{\mathrm{A}} = \lim_{R_{\mathrm{AB}}\to\infty} -\bar{Q}_{\mathrm{B}} = \frac{\chi^0_{\mathrm{B}} - \chi^0_{\mathrm{A}}}{2(\eta^0_{\mathrm{A}} + \eta^0_{\mathrm{B}})} \quad (8)$$

a quantity that is never zero (and even unphysical) in a heteronuclear molecule, where $\chi^0_{\mathrm{B}} \neq \chi^0_{\mathrm{A}}$ (For more details about the dissociation problem, see the discussion of Figures 1 and 2 in Section 2.B). Berkowitz[26] ingeniously corrected that wrong asymptotic behavior by enforcing the chemical equilibrium condition $\mu_{\mathrm{A}} = \mu_{\mathrm{B}}$ at all bond separations (The original SPEE enforces that condition only when all the atoms are closely bonded); however, the resulting equations[26] do not describe charge transfers as driven by electronegativity differences as eq 7 does. Contrastingly, a solution to the above asymptotic problem that still retains that conceptual electronegativity picture is advanced below in Section 2.B (See also refs 27 and 28 for other solutions in a similar spirit).

More recently, Morales and Martínez[13,27] demonstrated that the aforesaid deficiencies in the CE model partially stem from some heuristic assumptions employed in the traditional CE derivations. More importantly, those authors also demonstrated that a less heuristic, wave function-based approach to the CE model (i.e., an approach neither phenomenological nor DFT-based) can contribute to the solution of some CE deficiencies; that approach was based on the valence bond (VB)[29] theory. In that context, it was postulated that the introduction of the atomic overlap into the linear coefficient of the CE energy [cf., eq 34] may correct the CE dissociation problem since that new coefficient could regulate the interatomic charge transfers.[27] That postulated energy expression, then named: pairwise-electronegativity charge-constrained quadratic valence-bond model 2 (PE-CC-QVB2),[27] provided a satisfactory description of charge transfers at dissociation in $\mathrm{LiH}_{(g)}$[27] and $\mathrm{NaCl}_{(g)}$.[28] Those early efforts were the motivation of this investigation that, working within a larger theoretical scope, now provide a rigorous derivation of the postulated PE-CC-QVB2 model, among other findings. As a result, a novel VB/Coherent-States (CS)[30] approach to the CE model is presented herein. As its name indicates, this VB/CS approach combines for the first time two methodologies that have been hitherto unrelated; the first methodology is the VB theory that provides a localized electronic description to appropriately embark upon the CE model;[13,27] the second methodology is the CS theory that provides a rigorous justification for the classical-electrostatic features of the CE model as derived from the quantum VB theory. Thus, a main theoretical contribution in this investigation is the finding of a connection between the quantum and the classical-electrostatics features of the VB and CE descriptions, respectively, via the CS theory. The latter is possible because the novel VB CS sets involved in this approach comprise quantum states that obey classical electrodynamics (i.e., they exhibit quasi-classical behavior[30−32]). In fact, with those quasi-classical VB CS sets, the CE classical-electrostatics description of a molecule becomes analogous to that of a molecular electric circuit. That Q/C connection is also important to rigorously combine a CE-like model with a quantum method in a Q/C hybrid.

In keeping with its dual nature, this VB/CS approach is introduced in two papers, hereafter called Paper I (the present one) and Paper II (its sequel), that successively deal with the VB (Paper I) and the CS (Paper II) parts of this project. For presentation's sake, Papers I and II develop the VB/CS approach to the CE model only for neutral diatomic molecules without a Q/C partition. However, the proposed approach is not restricted to that diatomic case. In fact, the VB/CS treatment of cases involving polyatomic molecules and/or Q/C partitions will be presented in later papers in this series. The VB part of the VB/CS approach is developed in this, Paper I, as follows. In Section 2.A, a parent quantum VB model to describe intramolecular charge transfers in a neutral diatomic molecule is defined by a set of five rules. In Section 2.B, a generalized CE model is derived from the previous VB model by sequentially applying seven approximations; that generalized CE model overcomes some of the discussed CE deficiencies (imprecisely defined charges and Coulomb interactions, incorrect dissociations) while containing the traditional CE model as a subcase. The dissociation behavior of that generalized CE model is analyzed for the cases of $\mathrm{HF}_{(g)}$, $\mathrm{LiH}_{(g)}$ and $\mathrm{NaCl}_{(g)}$. In Section 2.C, a family of generalized CE models, including the previous model, is derived in order to gain further insight into the relationship between the VB and CE theories. That is completed in Section 2.D, where the equivalence between the energy and charge optimization procedures of all the derived CE models and the original VB eigenvector equations is demonstrated. The latter also proves that all of the generalized and traditional CE models implicitly involve VB wave functions despite their outwardly classical appearance. Finally, in Section 3, the conclusions are presented. The CS part of this VB/CS approach will be developed in Paper II, directly from the results of Paper I. However, this Paper I can be read independently from Paper II because it does not depend upon the latter's results. Therefore, a detailed discussion on the CS theory is not presented herein but in Paper II. Paper II will be submitted for publication soon.

2. Theory

A. The VB Model 3 for Neutral Diatomic Molecules. The VB/CS approach to the CE model starts with a parent VB model. The latter does not require the explicit treatment of all of the electrons in a molecule but only a few of them that capture the basic features of intramolecular charge transfers. The specific details of the parent VB model depend upon the type of molecule under description (diatomic, triatomic, polyatomic, etc.) and are determined by a set of rules. For neutral diatomic molecules, AB, that model is a three-state VB model for two effective electrons hereafter called the VB Model 3. The rules defining the VB Model 3 are:

- ***Rule I.*** Treat explicitly only one active valence electron per atom: $N_{\mathrm{A}} = N_{\mathrm{B}} = 1$, so that the total number of effective electrons is: $N_{\mathrm{el}}^{\mathrm{eff}} = N_{\mathrm{A}} + N_{\mathrm{B}} = 2$; then, consider the remaining valence and core electrons inactive by being part of frozen cores on the nuclear centers and rendering effective nuclear charges $Z_{\mathrm{A}}^{\mathrm{eff}}$ and $Z_{\mathrm{B}}^{\mathrm{eff}}$, $Z_{\mathrm{A}}^{\mathrm{eff}} + Z_{\mathrm{B}}^{\mathrm{eff}} = +2$.

Rule I prescribes a drastic core approximation[33] that seems tolerable for alkali metal atoms because their chemistry is dominated by their single ns^1 valence electrons; however, that approximation seems less acceptable for other types of atoms because it merges most of the valence electrons with those at the cores. Nonetheless, despite its crudeness, this core approximation effectively leads to the CE model as shown below.

- ***Rule II.*** Take the effective Hamiltonian $\hat{H}_{\mathrm{eff}}^{(3)}$ for the two effective electrons as the model Hamiltonian of molecule AB

$$\hat{\mathrm{H}}_{\mathrm{eff}}^{(3)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = \hat{H}(\mathbf{r}_1) + \hat{H}(\mathbf{r}_2) + \frac{1}{r_{12}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}} Z_{\mathrm{B}}^{\mathrm{eff}}}{R} \tag{9}$$

with

$$\hat{H}(\mathbf{r}_i) = \hat{T}(\mathbf{r}_i) + \hat{V}_{\mathrm{A}}(\mathbf{r}_i) + \hat{V}_{\mathrm{B}}(\mathbf{r}_i);$$

$$\hat{T}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2;\ \hat{V}_{\mathrm{A/B}}(\mathbf{r}_i) = -\frac{Z_{\mathrm{A/B}}^{\mathrm{eff}}}{|\mathbf{R}_{\mathrm{A/B}} - \mathbf{r}_i|};\ i = 1, 2 \tag{10}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of the effective electrons, $\mathbf{R}_{\mathrm{A}}$ and $\mathbf{R}_{\mathrm{B}}$ the positions of the nuclei, $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ and $R = |\mathbf{R}_B - \mathbf{R}_A|$ the separations between the electrons and the nuclei, respectively, and $\hat{T}(\mathbf{r}_i)$ and $\hat{V}_{\mathrm{A/B}}(\mathbf{r}_i)$ the electronic kinetic energy and nuclear potential operators, respectively. The symbol (3) in $\hat{H}_{\mathrm{eff}}^{(3)}$ and in subsequent expressions denotes the VB Model 3; it is written between parentheses to avoid confusing it with power exponents or superscripts.

- ***Rule III.*** Describe the two effective electrons in terms of a minimum basis set consisting of two atomic spin−orbitals per atom: $\{\phi_{\mathrm{A}}(\mathbf{r})\alpha(s), \phi_{\mathrm{A}}(\mathbf{r})\beta(s)\}$ and $\{\phi_{\mathrm{B}}(\mathbf{r})\alpha(s), \phi_{B}(\mathbf{r})\beta(s)\}$, where $\phi_{\mathrm{A/B}}(\mathbf{r})$ is a spatial atomic orbital, and $\alpha(s)/\beta(s)$ a one-electron spin eigenfunction.

Those atomic spin−orbitals are nonorthogonal: $S_{\mathrm{AB}}(R) = \langle\phi_{\mathrm{A}}|\phi_{\mathrm{B}}\rangle = \langle\bar{\phi}_{\mathrm{A}}|\bar{\phi}_{B}\rangle \neq 0$, where $S_{\mathrm{AB}}(R)$ is the atomic overlap at separation R, and the no-overbar/overbar denotes a α/β spin eigenfunction; notice that $S_{\mathrm{AB}}(R \rightarrow \infty) = 0$. Those atomic spin-orbitals will be considered as real functions. Examples of atomic spin-orbitals adequate for the CE model are discussed in the next section.

• ***Rule IV.*** For the model two-electron molecule AB, determine the covalent VB structure A−B and its corresponding VB state $\Psi_1^{(3)}$:

$$\Psi_1^{(3)} = \frac{1}{\sqrt{2(1+S_{\mathrm{AB}}{}^2)}}(|\phi_{\mathrm{A}}\bar{\phi}_{\mathrm{B}}\rangle - |\bar{\phi}_{\mathrm{A}}\phi_{\mathrm{B}}\rangle) \text{ (Covalent: A} - \text{B)} \tag{11}$$

where $|\cdots\rangle$ denotes a Slater determinant: $|\cdots\rangle = (N_{\mathrm{el}}!)^{-1/2}$ det$(\cdots)$ for an N_{el}-electron state.

• ***Rule V.*** Finally, generate the remaining VB structures and states of the VB Model 3 by effecting all of the possible heterolytic cleavages of the bond in the covalent VB structure A−B of Rule IV; that gives rise to the additional VB structures and states: ionic I $\mathrm{A}^+ \mathrm{B}^-$, $\Psi_2^{(3)}$; and ionic II $\mathrm{A}^- \mathrm{B}^+$, $\Psi_3^{(3)}$, respectively:

$$\begin{aligned}\Psi_2^{(3)} &= |\phi_{\mathrm{B}}\bar{\phi}_{\mathrm{B}}\rangle \text{ (Ionic I: A}^+\text{B}^-\text{);}\\ \Psi_3^{(3)} &= |\phi_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}\rangle \text{ (Ionic II: A}^-\text{B}^+\text{)}\end{aligned} \tag{12}$$

Conceptually, the three VB structures from Rules IV and V contain all of the possible rearrangements of the two effective electrons over the atoms A and B: A−B, $\mathrm{A}^+ \mathrm{B}^-$ and $\mathrm{A}^- \mathrm{B}^+$, from which the CE charge transfers will be derived. The Rules I−V for diatomic molecules have been presented in a systematic and abstract way because in that form they can be easily extended to more complex cases with polyatomic molecules. The resulting VB Model 3, representing an idealized two-electron, single-bonded molecule without extra lone pairs and/or unpaired electrons, leads to the CE description for any molecule AB, as shown below. This is so, even if the actual electronic structure of that molecule (e.g., more than two electrons, double or triple bonds, lone pairs, etc.) does not correspond to that simplified representation. More realistic VB models starting from covalent VB structures: A═B or A≡B, including lone pairs and/or unpaired electrons if appropriate, and implying various ionic VB structures, lead to more sophisticated forms of the CE model that will be analyzed in the future.

Given the Rules I−V, the VB Model 3 can be developed by following usual VB prescriptions.[29,34] A trial VB Model 3 wave function $\Psi_{\mathrm{VB}}^{(3)}$ is:

$$\Psi_{\mathrm{VB}}^{(3)} = c_1^{(3)}\Psi_1^{(3)} + c_2^{(3)}\Psi_2^{(3)} + c_3^{(3)}\Psi_3^{(3)} \tag{13}$$

where $c_1^{(3)}$, $c_2^{(3)}$ and $c_3^{(3)}$ are the VB variational coefficients that are taken as real because a real atomic basis set is assumed. The VB energy $E_{\mathrm{VB}}^{(3)}$ and VB normalization condition of $\Psi_{\mathrm{VB}}^{(3)}$ are as follows:

$$\begin{aligned}E_{\mathrm{VB}}^{(3)} &= \langle\Psi_{\mathrm{VB}}^{(3)}|\hat{H}_{\mathrm{eff}}^{(3)}|\Psi_{\mathrm{VB}}^{(3)}\rangle = c_1^{(3)2}H_{11}^{(3)} + c_2^{(3)2}H_{22}^{(3)} + c_3^{(3)2}H_{33}^{(3)} +\\ &\quad 2c_1^{(3)}c_2^{(3)}H_{12}^{(3)} + 2c_1^{(3)}c_3^{(3)}H_{13}^{(3)} + 2c_2^{(3)}c_3^{(3)}H_{23}^{(3)};\\ 1 &= \langle\Psi_{\mathrm{VB}}^{(3)}|\Psi_{\mathrm{VB}}^{(3)}\rangle = c_1^{(3)2} + c_2^{(3)2} + c_3^{(3)2} + 2c_1^{(3)}c_2^{(3)}S_{12}^{(3)} +\\ &\quad 2c_1^{(3)}c_3^{(3)}S_{13}^{(3)} + 2c_2^{(3)}c_3^{(3)}S_{23}^{(3)}\end{aligned} \tag{14}$$

where $H_{ij}^{(3)}(R) = \langle\Psi_i^{(3)}|\hat{H}_{\mathrm{eff}}^{(3)}|\Psi_j^{(3)}\rangle$ and $S_{ij}^{(3)}(R) = \langle\Psi_i^{(3)}|\Psi_j^{(3)}\rangle$ are the VB energy and the VB overlap matrix elements, respectively, that are obtained via Löwdin Rules:[29]

$$\begin{aligned}H_{11}^{(3)} &= \frac{1}{(1+S_{\mathrm{AB}}{}^2)}\Big[h_{\mathrm{AA}} + h_{\mathrm{BB}} + J_{\mathrm{AB}} + K_{\mathrm{AB}} + V_{\mathrm{AA}}^{\mathrm{B}} + V_{\mathrm{BB}}^{\mathrm{A}} +\\ &\quad 2h_{\mathrm{AB}}^{\mathrm{AB}}S_{\mathrm{AB}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}(1+S_{\mathrm{AB}}{}^2)}{R}\Big] = \frac{1}{(1+S_{\mathrm{AB}}{}^2)}[E_{\mathrm{A}}^0 + E_{\mathrm{B}}^0 + F_{11}^{(3)}(R)];\\ H_{22}^{(3)} &= 2h_{\mathrm{BB}} + J_{\mathrm{BB}} + 2V_{\mathrm{BB}}^{\mathrm{A}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}}{R} = E_{\mathrm{A}}^+ + E_{\mathrm{B}}^- + F_{22}^{(3)}(R);\\ H_{33}^{(3)} &= 2h_{\mathrm{AA}} + J_{\mathrm{AA}} + 2V_{\mathrm{AA}}^{\mathrm{B}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}}{R} = E_A^- + E_B^+ + F_{33}^{(3)}(R);\\ H_{12}^{(3)} &= \frac{2}{\sqrt{2(1+S_{\mathrm{AB}}{}^2)}}\Big[h_{\mathrm{AB}}^{\mathrm{AB}} + (h_{\mathrm{BB}} + V_{\mathrm{BB}}^{\mathrm{A}})S_{\mathrm{AB}} + J_{\mathrm{AB}}^{\mathrm{BB}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}S_{\mathrm{AB}}}{R}\Big]\\ H_{13}^{(3)} &= \frac{2}{\sqrt{2(1+S_{\mathrm{AB}}{}^2)}}\Big[h_{\mathrm{AB}}^{\mathrm{AB}} + (h_{\mathrm{AA}} + V_{\mathrm{AA}}^{B})S_{\mathrm{AB}} + J_{\mathrm{AB}}^{\mathrm{AA}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}S_{\mathrm{AB}}}{R}\Big]\\ H_{23}^{(3)} &= 2h_{\mathrm{AB}}^{\mathrm{AB}}S_{\mathrm{AB}} + K_{\mathrm{AB}} + \frac{Z_{\mathrm{A}}^{\mathrm{eff}}Z_{\mathrm{B}}^{\mathrm{eff}}(1+S_{\mathrm{AB}}{}^2)}{R}\end{aligned} \tag{15}$$

where the atomic matrix elements are as follows:

$$\begin{aligned}h_{\mathrm{AA}} &= \langle\phi_{\mathrm{A}}|\hat{T} + \hat{V}_{\mathrm{A}}|\phi_{\mathrm{A}}\rangle;\\ h_{\mathrm{AB}}^{\mathrm{AB}} &= \langle\phi_{\mathrm{A}}|\hat{T} + \hat{V}_{\mathrm{A}} + \hat{V}_{\mathrm{B}}|\phi_{\mathrm{B}}\rangle;\\ V_{\mathrm{AA}}^{\mathrm{B}} &= \langle\phi_{\mathrm{A}}|\hat{V}_{\mathrm{B}}|\phi_{\mathrm{A}}\rangle;\ J_{\mathrm{AA}} = (\phi_{\mathrm{A}}\phi_{\mathrm{A}}|\phi_{\mathrm{A}}\phi_{\mathrm{A}});\\ J_{\mathrm{AB}}^{\mathrm{AA}} &= (\phi_{\mathrm{A}}\phi_{\mathrm{B}}|\phi_{\mathrm{A}}\phi_{\mathrm{A}});\ K_{\mathrm{AB}} = (\phi_{\mathrm{A}}\phi_{\mathrm{B}}|\phi_{\mathrm{B}}\phi_{\mathrm{A}})\end{aligned} \tag{16}$$

with analogous expressions for h_{BB}, $V_{\mathrm{BB}}^{\mathrm{A}}$, J_{BB}, and $J_{\mathrm{AB}}^{\mathrm{BB}}$. In the present description, an isolated atom A(B) can accommodate zero, one, or two effective electrons and thus generates its successive charged species with their corresponding wave functions: A^+ (B^+): $|\rangle$ (vacuum state, no electrons); A^0 (B^0): $|\phi_{\mathrm{A}}\rangle$ and $|\bar{\phi}_{\mathrm{A}}\rangle$ ($|\phi_{\mathrm{B}}\rangle$ and $|\bar{\phi}_{\mathrm{B}}\rangle$); and A^- (B^-): $|\phi_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}\rangle$($|\phi_{\mathrm{B}}\bar{\phi}_{\mathrm{B}}\rangle$). Therefore, the energies: E_{A}^+, E_{A}^0, E_{A}^-, E_{B}^+, E_{B}^0, and E_{B}^- of the charged species in eq 15 are as follows:

$$\begin{aligned}&E_{\mathrm{A}}^+ = 0;\ E_{\mathrm{B}}^+ = 0;\ E_{\mathrm{A}}^0 = \langle\phi_{\mathrm{A}}|\hat{T} + \hat{V}_{\mathrm{A}}|\phi_{\mathrm{A}}\rangle = h_{\mathrm{AA}};\\ &E_{\mathrm{B}}^0 = \langle\phi_{\mathrm{B}}|\hat{T} + \hat{V}_{\mathrm{B}}|\phi_{\mathrm{B}}\rangle = h_{\mathrm{BB}};\\ &E_{\mathrm{A}}^- = \langle\phi_{\mathrm{A}}\phi_{A}|\hat{H}_{\mathrm{eff}}^{(3)}|\phi_{\mathrm{A}}\phi_{\mathrm{A}}\rangle = 2h_{\mathrm{AA}} + J_{\mathrm{AA}};\\ &E_{\mathrm{B}}^- = \langle\phi_{\mathrm{B}}\phi_{\mathrm{B}}|\hat{H}_{\mathrm{eff}}^{(3)}|\phi_{\mathrm{B}}\phi_{\mathrm{B}}\rangle = 2h_{\mathrm{BB}} + J_{\mathrm{BB}}\end{aligned} \tag{17}$$

Then, the VB Model 3 ionization potential $\mathrm{IP}_{\mathrm{A}} = E_{\mathrm{A}}^+ - E_{\mathrm{A}}^0$, electron affinity $\mathrm{EA}_{\mathrm{A}} = E_{\mathrm{A}}^0 - E_{\mathrm{A}}{}^-$, Mulliken electronegativity χ_A^0, eq 2, and absolute hardness η_A^0, eq 2, for atom A are as follows:

$$\begin{aligned}&\mathrm{IP}_{\mathrm{A}} = -h_{\mathrm{AA}};\ \mathrm{EA}_{\mathrm{A}} = -h_{\mathrm{AA}} - J_{\mathrm{AA}};\\ &\chi_{\mathrm{A}}^0 = -h_{\mathrm{AA}} - \frac{1}{2}J_{\mathrm{AA}};\ \eta_{\mathrm{A}}^0 = \frac{1}{2}J_{\mathrm{AA}}\end{aligned} \tag{18}$$

with analogous expressions for atom *B*. In eq 15, $F_{ii}^{(3)}(R)$ are interaction functions in terms of two-center matrix elements:

$$F_{11}^{(3)}(R) = J_{AB} + K_{AB} + V_{AA}^{B} + V_{BB}^{A} + 2h_{AB}^{AB}S_{AB} + \frac{Z_A^{eff}Z_B^{eff}(1 + S_{AB}^2)}{R};$$
$$F_{22}^{(3)}(R) = 2V_{BB}^{A} + \frac{Z_A^{eff}Z_B^{eff}}{R};$$
$$F_{33}^{(3)}(R) = 2V_{AA}^{B} + \frac{Z_A^{eff}Z_B^{eff}}{R} \qquad (19)$$

Those functions describe the interaction between the atomic fragments. For instance, by setting $Z_A^{eff} = Z_B^{eff} = +1$ and the asymptotic values of the atomic matrix elements when $R \rightarrow$ Large: $J_{AB} \rightarrow 1/R$, $V_{AA}^{B} \rightarrow -1/R$, $V_{BB}^{A} \rightarrow -1/R$, $K_{AB} \rightarrow 0$ and $S_{AB} \rightarrow 0$, the interaction functions $F_{ii}^{(3)}(R)$ become: $F_{11}^{(3)}(R) \rightarrow 0$ and $F_{22}^{(3)}(R) = F_{33}^{(3)}(R) \rightarrow -1/R$ near dissociation. Those limits are the Coulomb law interactions between the atomic fragments in the three possible dissociations in the present model: A^0/B^0, A^+/B^-, and A^-/B^+, respectively.

Finally, the VB overlap matrix elements are as follows:

$$S_{11}^{(3)} = S_{22}^{(3)} = S_{33}^{(3)} = 1;\ S_{12}^{(3)} = S_{13}^{(3)} = \frac{2S_{AB}}{\sqrt{2(1+S_{AB}{}^2)}};\ S_{23}^{(3)} = S_{AB}{}^2 \qquad (20)$$

Since atomic charges are central to the CE model, attention should also be paid to the charge descriptions in the VB Model 3. Various definitions of electron population analyses[22,29] and atomic charges[22−25,29] exist but that by Mulliken[21,22] is the most useful herein. The VB Model 3 total ($\alpha + \beta$) Mulliken population requires the total density matrix $\mathbf{P}^{(3)} = (P_{AB}^{(3)})$ of $\Psi_{VB}^{(3)}$

$$P_{A/B\ A/B}^{(3)} = \left[\frac{c_1^{(3)2}}{(1+S_{AB}{}^2)} + 2c_{3/2}^{(3)2} + \frac{4c_1^{(3)}c_{3/2}^{(3)}S_{AB}}{\sqrt{2(1+S_{AB}{}^2)}}\right];$$
$$P_{AB}^{(3)} = \left[\frac{c_1^{(3)2}S_{AB}}{(1 + S_{AB}{}^2)} + \frac{2c_1^{(3)}(c_2^{(3)} + c_3^{(3)})}{\sqrt{2(1+S_{AB}{}^2)}} + c_2^{(3)}c_3^{(3)}S_{AB}\right] \qquad (21)$$

Then, the total Mulliken number of electrons $N_A^{(Mull)}$ $(= 2 - N_B^{(Mull)})$ and charge $Q_A^{(Mull)}(= -Q_B{}^{(Mull)})$ on atom A are as follows:[21,22]

$$N_A^{(Mull)} = \sum_{C\in A}\sum_{D=A,B} P_{CD}^{(3)}S_{DC}^{(3)} = c_1^{(3)2} + 2c_3^{(3)2} + \frac{6c_1^{(3)}c_3^{(3)}S_{AB}}{\sqrt{2(1+S_{AB}{}^2)}} + \frac{2c_1^{(3)}c_2^{(3)}S_{AB}}{\sqrt{2(1 + S_{AB}{}^2)}} + 2c_2^{(3)}c_3^{(3)}S_{AB}{}^2;\ \ Q_A^{(Mull)} = Z_A^{eff} - N_A^{(Mull)} \qquad (22)$$

The standard VB procedure[29,34] for the VB Model 3 involves applying the linear variational principle[34] to the variational integral $E_{VB}^{(3)}/\langle\Psi_{VB}^{(3)}|\Psi_{VB}^{(3)}\rangle$ to determine the optimal trial function $\Psi_{VB}^{(3)}$; that leads to the VB eigenvector equation[29,34]

$$\begin{pmatrix} H_{11}^{(3)} - E_i^{(3)} & H_{12}^{(3)} - S_{12}^{(3)}E_i^{(3)} & H_{13}^{(3)} - S_{13}^{(3)}E_i^{(3)} \\ H_{12}^{(3)} - S_{12}^{(3)}E_i^{(3)} & H_{22}^{(3)} - E_i^{(3)} & H_{23}^{(3)} - S_{23}^{(3)}E_i^{(3)} \\ H_{13}^{(3)} - S_{13}^{(3)}E_i^{(3)} & H_{23}^{(3)} - S_{23}^{(3)}E_i^{(3)} & H_{33}^{(3)} - E_i^{(3)} \end{pmatrix}\begin{pmatrix} c_{1i}^{(3)} \\ c_{2i}^{(3)} \\ c_{3i}^{(3)} \end{pmatrix} = 0; \quad i = 1, 2, 3 \qquad (23)$$

and associated secular equation that provide three eigenvectors/eigenvalues:$(c_{1i}^{(3)}, c_{2i}^{(3)}, c_{3i}^{(3)})^T / E_i{}^{(3)}$ corresponding to the ground and first two excited states. From those solutions, it is easy to corroborate that the VB Model 3 correctly describes the charge transfers during the gas-phase dissociation of a ground-state molecule AB. At $R \rightarrow \infty$, the matrix in eq 23 becomes diagonal (cf., eqs 15 and 20) so that its asymptotic eigenvalues are as follows: $E_1^{(3)} = E_A^0 + E_B^0$, $E_2^{(3)} = E_A^+ + E_B^- = E_A^0 + E_B^0 + IP_A - EA_B$, and $E_3^{(3)} = E_A^- + E_B^+ = E_A^0 + E_B^0 + IP_B - EA_A$, which correspond to the VB wave functions: $\Psi_{VB\ 1}^{(3)} = \Psi_1^{(3)}$, $\Psi_{VB\ 2}^{(3)} = \Psi_2^{(3)}$, and $\Psi_{VB\ 3}^{(3)} = \Psi_3^{(3)}$, which represent the fragmentations: $A_{(g)}^0 + B_{(g)}^0$, $A_{(g)}^+ + B_{(g)}^-$, and $A_{(g)}^- + B_{(g)}^+$, respectively. Provided with standard CE parametrizations,[2,14] the VB Model 3 can reproduce the experimental condition $IP_{A/B} - EA_{B/A} > 0$ so that $E_1^{(3)} = E_{A^0B^0} <$ both $E_2^{(3)} = E_{A^+B^-}$ and $E_3{}^{(3)} = E_{A^-B^+}$, which correctly favors the dissociation into uncharged species at the ground state.

The three-state VB Model 3 is central to this investigation but additional VB submodels are necessary in subsequent discussions. Two of those submodels are the two-state VB Models 2− and 2+ in terms of the VB-related functions $\{\Psi_1^{(2-)}, \Psi_2^{(2-)}\}$ and $\{\Psi_1^{(2+)}, \Psi_2^{(2+)}\}$, respectively,

$$\Psi_1^{(2-)} = \Psi_1^{(2+)} = \Psi_1^{(3)};\ \Psi_2^{(2-)} = \frac{(\Psi_2^{(3)} - \Psi_3^{(3)})}{\sqrt{2(1-S_{AB}{}^2)}};$$
$$\Psi_2^{(2+)} = \frac{(\Psi_2^{(3)} + \Psi_3^{(3)})}{\sqrt{2(1+S_{AB}{}^2)}} \qquad (24)$$

While $\Psi_1^{(2-)}$ and $\Psi_1^{(2+)}$ correspond to the VB covalent A−B state $\Psi_1^{(3)}$, $\Psi_2^{(2-),}$ and $\Psi_2^{(2+)}$ do not correspond to any genuine VB state because both mix the ionic I A^+ B^- $\Psi_2^{(3)}$ and ionic II A^- B^+ VB $\Psi_3^{(3)}$ states; the latter implies that the VB Models 2− and 2+ are not VB models, strictly speaking. However, those models will be termed "VB" because their states are directly related to the genuine VB states of the VB Model 3, eq 24. The energy and overlap matrix elements of the VB Models 2− and 2+: $H_{ij}^{(2\pm)}(R)$ and $S_{ij}^{(2\pm)}(R)$, are also related to their VB Model 3 equivalents. For instance, their VB overlap matrix elements are as follows:

$$S_{11}^{(2\pm)} = S_{11}^{(3)} = 1;\ S_{12}^{(2-)} = (S_{12}^{(3)} - S_{13}^{(3)})/\sqrt{2(1 - S_{AB}{}^2)} = 0;$$
$$S_{12}^{(2+)} = (S_{12}^{(3)} + S_{13}^{(3)})/\sqrt{2(1+S_{AB}{}^2)} = 2S_{AB}/(1 + S_{AB}{}^2) \qquad (25)$$

Notice that the VB Model 2− is orthogonal.

B. The VB Generalized CE Model from the VB Model 3. The VB Model 3 is a minimal quantum method that can provide a meaningful description of intramolecular charge transfers; however, that model still differs from the targeted CE model. For instance, the VB Model 3 energy, eq 14, is a function of *two* independent VB coefficients (after normalization is considered) that are obtained via the VB eigenvector eq 23; contrastingly, the CE energy, eq 5, is a function of *one* independent atomic charge Q_A (after conservation of total charge is considered) that is obtained via the classical SPEE CE eq 7. Despite those dissimilarities, a VB generalized CE model (VB/GCE) can be derived from the VB Model 3 by sequentially applying to the latter the approximations discussed below. Those approximations are similar to well-known approximations used in semiempirical methods[33] and in CE models.[13,27,35] In this context, the aim of the prescribed approximations is to transform the quantum description of the VB Model 3 into the classical-electrostatics description of the CE and VB/GCE models. The approximations are as follows:

- ***Approximation I.*** First, introduce a 2 × 2 charge matrix $\mathbf{q}$[35]:

$$\mathbf{q} = \begin{pmatrix} q_{AA} & q_{AB} \\ q_{BA} & q_{BB} \end{pmatrix} \tag{26}$$

where the charge variable element q_{CD} (C, D = A, B) is defined as the amount of charge that atom C interchanges with atom D; then, it follows that $\mathbf{q}$ is skew-symmetric because $q_{CD} = -q_{DC}$ by charge conservation, and that $q_{CC} = -q_{CC} = 0$ because an atom has a zero charge interchange with itself. Then, by taking q_{AB} ($= -q_{BA}$) as the only independent charge variable, map the VB variational coefficients $\{c_1^{(3)}, c_2^{(3)}, c_3^{(3)}\}$ into q_{AB} as follows:

$$c_2^{(3)}(q_{AB}) = -c_3^{(3)}(q_{AB}) = \frac{q_{AB}}{\sqrt{2}} \tag{27}$$

where $c_1^{(3)}(q_{AB})$ can be obtained from $c_2^{(3)}(q_{AB})$ and $c_3^{(3)}(q_{AB})$ via the normalization condition, eq 14 [See eq A1, Appendix].

This map imposes a constraint on the VB coefficients that along with the normalization condition leaves only *one* independent variable in the VB Model 3, as is the case of the CE model for neutral diatomic molecules.

- ***Approximation II.*** Neglect all the terms having $S_{AB}^n(R)$ with $n \geq 1$ in the VB normalization condition.
- ***Approximation III.*** To all the two-center VB atomic integrals $\langle \phi_A | \hat{O} | \phi_B \rangle$ ($A \neq B$) in eq 16 that do *not* occur in CE energy expressions, eqs 5 and 6, apply the Mulliken Approximation:[33]

$$\langle \phi_A | \hat{O} | \phi_B \rangle = \frac{1}{2}[\langle \phi_A | \hat{O} | \phi_A \rangle + \langle \phi_B | \hat{O} | \phi_B \rangle] S_{AB} \tag{28}$$

where $\hat{O}$ is the operator in the integral. This approximation applies to: h_{AB}^{AB}, J_{AB}^{AA}/J_{AB}^{BB} and K_{AB}, for which $\hat{O} = \hat{H} = \hat{T} + \hat{V}_A + \hat{V}_B$, $\hat{O}(1) = \hat{J}_{A/B}(1) = \int d\mathbf{r}_2 |\phi_{A/B}(\mathbf{r}_2)|^2 r_{12}^{-1}$, and $\hat{O}(1) = \int d\mathbf{r}_2 \phi_B(\mathbf{r}_2)\phi_A(\mathbf{r}_2) r_{12}^{-1}$, respectively, so that,

$$h_{AB}^{AB} = \frac{1}{2}(h_{AA} + h_{BB} + V_{AA}^{B} + V_{BB}^{A}) S_{AB};$$
$$J_{AB}^{BB} = \frac{1}{2}(J_{BB} + J_{AB}) S_{AB};\ J_{AB}^{AA} = \frac{1}{2}(J_{AA} + J_{AB}) S_{AB};$$
$$K_{AB} = \frac{1}{2}\left[J_{AB} + \frac{1}{2}(J_{AA} + J_{BB})\right] S_{AB}^{\ 2} \text{ (Approx. III)} \tag{29}$$

Notice that for K_{AB}, this approximation should be applied thrice to obtain the above result.

- ***Approximation IV.*** In all the off-diagonal VB energy matrix elements and in the Mulliken population expressions, eq 22, approximate the denominator $\sqrt{1+S_{AB}^2(R)}$ to a constant "average" value $2S_{AB}^0$

$$\sqrt{1 + S_{AB}^2(R)} = 2S_{AB}^0 \text{ (Approx. IV)} \tag{30}$$

where S_{AB}^0 is a value of the overlap $S_{AB}(R)$ at a chosen separation $R = R_0$. S_{AB}^0 is an adjustable parameter whose specific value is determined below.

- ***Approximation V.*** Neglect all the terms having $S_{AB}^n(R)$ with $n \geq 2$ in the rest of the VB expressions.
- ***Approximation VI.*** Neglect all the terms having $q_{CD}{}^n$ (C, D = A, B) with $n \geq 3$ in all the resulting VB expressions so that they become quadratic functions of q_{CD} at most.

This approximation is acceptable when the intramolecular charge transfers are relatively low: $|q_{CD}|$ much smaller than $1\bar{e}$, as is the case during most applications of the CE model.

- ***Approximation VII.*** Define the VB/GCE atomic charges Q_A and Q_B in the resulting VB expressions as follows:

$$Q_A = \sum_{C=A}^{B} q_{AC} = q_{AA} + q_{AB};\ Q_B = \sum_{C=A}^{B} q_{BC} = q_{BB} + q_{BA} \tag{31}$$

where the skew-symmetric matrix $\mathbf{q}$ correctly enforces that $Q_A + Q_B = 0$.

Like with Rules I−V, the Approximations I−VII for neutral diatomic molecules have been presented in a systematic and abstract way because in that form they can be easily extended to more complex cases with polyatomic molecules. For instance, in a triatomic molecule ABC, a 3 × 3 skew-symmetric matrix $\mathbf{q}$ is employed from which $Q_A = q_{AA} + q_{AB} + q_{AC}$.

The application of Approximations I−VII to the VB Model 3 energy $E_{VB}^{(3)}$, eq 14, to obtain the VB/GCE model energy $E_{AB}^{VB/GCE}$ is lengthy and is therefore given in the Appendix. As shown there, $E_{VB}^{(3)}$ is transformed into the VB/GCE energy $E_{AB}^{VB/GCE}$: $E_{VB}^{(3)} = E_{AB}^{VB/GCE}$, where

$$E_{AB}^{VB/GCE}(Q_A) = A^{VB/GCE} + B^{VB/GCE} Q_A + C^{VB/GCE} Q_A^{\ 2} \tag{32}$$

with

$$A^{VB/GCE} = E_{A^0} + E_{B^0} + F_{11}^{(3)}(R) = H_{11}^{(3)};$$
$$B^{VB/GCE} = (\chi_A^* - \chi_B^*)\bar{S}_{AB} = \sqrt{2}(H_{12}^{(3)} - H_{13}^{(3)});$$
$$C^{VB/GCE} = \eta_A^0 + \eta_B^0 - J_{AB} = \frac{1}{2}(H_{22}^{(3)} + H_{33}^{(3)} - 2H_{11}^{(3)}) \tag{33}$$

where $\bar{S}_{AB}(R) = S_{AB}(R)/S_{AB}^0$ is a generalized overlap; an equivalent form of $E_{AB}^{VB/GCE}(Q_A)$, eq 32, akin to eq 3, is,

$$E_{AB}^{VB/GCE}(Q_A, Q_B) = E_A^0 + E_B^0 + F_{11}^{(3)} + \chi_A^* \bar{S}_{AB} Q_A + \chi_B^* \bar{S}_{AB} Q_B + \eta_A^0 Q_A^{\ 2} + \eta_B^0 Q_B^{\ 2} + J_{AB} Q_A Q_B \tag{34}$$

Similarly, with Approximations I−VII, the VB Model 3 Mulliken number of electrons $N_A^{(Mull)}$ and charge $Q_A^{(Mull)}$ become (See Appendix):

$$N_A^{(Mull)} = 1 - Q_A \bar{S}_{AB};\ Q_A^{(Mull)} = Q_A \bar{S}_{AB}\ (Z_A^{eff} = +1) \tag{35}$$

The energy expression in eq 34 is equivalent to the postulated PE-CC-QVB2 energy expression from ref 27; thus, the present derivation provides a rigorous theoretical justification for the hypothesized PE-CC-QVB2 model.

Conceptually, the contribution of each approximation to obtain the above results is as follows: The map in Approximation I reduces the two independent VB Model 3 coefficients to only one independent variable (q_{AB}) as is the case of the CE model for diatomic molecules. Approximation III permits expressing many two-center atomic integrals $\langle \phi_A | \hat{O} | \phi_B \rangle$ in terms of one-center integrals $\langle \phi_A | \hat{O} | \phi_A \rangle$ and $\langle \phi_B | \hat{O} | \phi_B \rangle$ and the overlap $S_{AB}(R)$. That splitting allows deconstructing the VB Model 3 energy into separated atomic terms that can be reconstructed into the VB/GCE energy by the successive approximations. Approximations II, IV, and V further simplify the VB Model 3 expressions toward a CE format. Approximation VI transforms the VB Model 3 energy into a quadratic function of a charge variable (q_{AB}) that resembles the CE energy. Finally, Approximation VII defines the VB/GCE charges and brings about the final $E_{AB}^{VB/GCE}$ expression. It is worth noticing that the independent $A^{VB/GCE}$ and quadratic $C^{VB/GCE}$ coefficients in $E_{AB}^{VB/GCE}$ come from the diagonal VB Model 3 energy matrix elements, whereas the linear coefficient $B^{VB/GCE}$ comes from the off-diagonal VB ones. The treatment of the atomic overlap integrals via Approximations II and V in this derivation is equivalent to

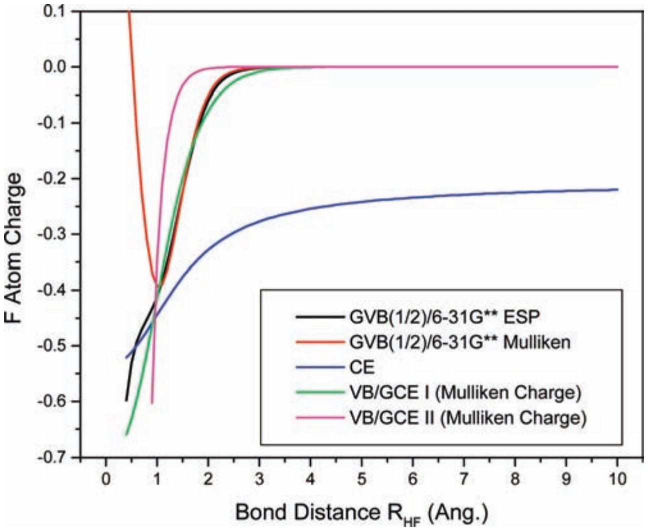

Figure 2. The same as in Figure 1 except that for VB/GCE I and II, their VB Model 3 Mulliken charges, eq 35, are shown instead.

treatments employed in semiempirical methods;[33] the same treatment of the overlap integrals was also employed in a previous CE investigation with the VB theory[13] and provided meaningful results. In some semiempirical methods, and in this derivation, overlap integrals are dropped from some expressions (e.g., in the normalization) because such a neglect does not seriously affect the final results; conversely, overlap integrals are retained in other expressions (e.g., in some atomic integrals of the energy) because if neglected, they can seriously affect the final results. For instance, in the complete neglect of differential overlap (CNDO) method,[33] overlap integrals S_{AB} are neglected in the normalization condition, but they are retained in the resonance integrals $H_{\mathrm{AB}} = (1/2)\ (\beta_{\mathrm{A}} + \beta_{\mathrm{B}})S_{\mathrm{AB}}$ of the energy and the Fock matrix; notice that those retained CNDO resonance integrals are equivalent to the first retained integral in eq 29 in this derivation, and that all those integrals are evaluated with the Mulliken Approximation prescribed in Approximation III. Also, in the Hückel method,[33] overlap integrals S_{AB} are neglected in the normalization condition, whereas resonance integrals $\beta \propto S_{\mathrm{AB}}$ are retained in the energy and other expressions. Here, overlap integrals are neglected in the normalization condition, but they are retained in some atomic integrals in eq 29 occurring in the energy and other expressions because, in the present scheme, those retained integrals become analogous to the retained integrals in CNDO and Hückel.

The CE energy $E_{\mathrm{AB}}^{\mathrm{CE}}$, eqs 5 and 6, is a subcase of the VB/GCE energy $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$, eqs 32 and 33, that is obtained from the latter if two more approximations are applied:

- ***Approximation VIII.*** Neglect the interaction function $F_{11}^{(3)}(R)$, $F_{11}^{(3)}(R) \approx 0$.
- ***Approximation IX.*** Assume that $\bar{S}_{\mathrm{AB}}(R) = S_{\mathrm{AB}}(R)/S_{\mathrm{AB}}^{0} = 1$ at all separations R.

Approximation VIII is plausible because the neutral atoms' interaction $F_{11}^{(3)}(R)$ is weak. Approximation IX is only exact at an R_0 where $S_{\mathrm{AB}}(R_0) = S_{\mathrm{AB}}^{0}$. Therefore, a convenient selection of the VB/GCE parameter S_{AB}^{0} is the atomic overlap at the equilibrium bond distance $R_{\mathrm{Eq.}}$, $S_{\mathrm{AB}}^{0} = S_{\mathrm{AB}}(R_{\mathrm{Eq.}})$, because that choice makes $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$, eq 32, identical to $E_{\mathrm{AB}}^{\mathrm{CE}}$, eq 5, at a separation where the latter behaves correctly; that selection for S_{AB}^{0} will be adopted henceforth. Under those conditions, eq 35 finally elucidates that the CE charge Q_{A} is the Mulliken charge $Q_{\mathrm{A}}^{(\mathrm{Mull})}$ of the underlying VB Model 3 subject to Approximations I–IX. Also, the factor J_{AB} of the Coulomb interaction: $J_{\mathrm{AB}}Q_{\mathrm{A}}Q_{\mathrm{B}} = -J_{\mathrm{AB}}Q_{\mathrm{A}}{}^{2}$ in eqs 32–34 is no longer an ad-hoc term because it has been derived from the interaction functions $F_{ii}^{(3)}(R)$ via a subtle cancelation of terms in eq A6 (See Appendix).

$E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$ exhibits two improvements over $E_{\mathrm{AB}}^{\mathrm{CE}}$. First, the neutral atoms' energy $A^{\mathrm{VB/GCE}} = E_{\mathrm{A}^0} + E_{\mathrm{B}^0} + F_{11}^{(3)}(R)$ correctly includes the neutral atoms' interaction $F_{11}^{(3)}(R)$, which is absent in $A^{\mathrm{CE}} = E_{\mathrm{A}^0} + E_{\mathrm{B}^0}$; that inclusion makes $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$ more realistic than $E_{\mathrm{AB}}^{\mathrm{CE}}$ but does not affect the charge description because both $A^{\mathrm{VB/GCE}}$and A^{CE} are the independent coefficients in their energy expressions. Second, and more importantly, $B^{\mathrm{VB/GCE}} = (\chi_{\mathrm{A}}^{*} - \chi_{\mathrm{B}}^{*})\bar{S}_{\mathrm{AB}}$ contains the extra term $\bar{S}_{\mathrm{AB}}(R) = S_{\mathrm{AB}}(R)/S_{\mathrm{AB}}{}^{0}$ that modulates the electronegativity difference during charge transfers. The optimal VB/GCE charge $\bar{Q}_{\mathrm{A}}$ $(= -\bar{Q}_{\mathrm{B}})$ from $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$, eq 32, is,

$$\bar{Q}_{\mathrm{A}} = -\bar{Q}_{\mathrm{B}} = -\frac{B^{\mathrm{VB/GCE}}}{2C^{\mathrm{VB/GCE}}} = \frac{[\chi_{\mathrm{B}}^{0} - \chi_{\mathrm{A}}^{0} + \int \hat{V}_{\mathrm{B}}(\mathbf{r})f_{\mathrm{A}}(\mathbf{r})d\mathbf{r} - \int \hat{V}_{\mathrm{A}}(\mathbf{r})f_{\mathrm{B}}(\mathbf{r})d\mathbf{r}]\bar{S}_{\mathrm{AB}}(R)}{2[\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0} - J_{\mathrm{AB}}^{\mathrm{CE}}(R_{\mathrm{AB}})]} \tag{36}$$

where the charge transfer leading to those optimal charges is portrayed as driven by the electronegativity difference in $B^{\mathrm{VB/GCE}} = (\chi_{\mathrm{A}}^{*} - \chi_{\mathrm{B}}^{*})\bar{S}_{\mathrm{AB}}$. Equation 36 correctly predicts that $\bar{Q}_{\mathrm{A}} = -\bar{Q}_{\mathrm{B}} = 0$ at $R \rightarrow \infty$ because in that case $\bar{S}_{\mathrm{AB}} \rightarrow 0$. This correct asymptotic behavior arises from the vanishing of $B^{\mathrm{VB/GCE}}$ at large R; $B^{\mathrm{VB/GCE}}$ inherits that asymptotic behavior from its built-in, off-diagonal VB energy matrix elements, eq 33 (See Appendix).

The correct behavior of the VB/GCE model is further illustrated by two numerical tests of the VB/GCE atomic charges in $\mathrm{HF}_{(g)}$ shown in Figures 1 and 2. Like in seminal CE investigations,[2,14] the present tests concentrate on the charge description of the VB/GCE model. While a specific VB/GCE parametrization of $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}$ is not available yet, it suffices herein to borrow the CE parameters of Goddard and Rappé,[2] and of Itskowitz and Berkowitz[14] (See Table 1) and obtain the VB/GCE I and II parametrizations, respectively. In both cases, the spatial atomic orbitals $\{\phi_A(\mathbf{r})\}$ are s-type Slater orbitals $\phi_{\mathrm{A}}(\mathbf{r}) = N_{n_{\mathrm{A}}}r^{n_{\mathrm{A}}1}\exp(-\zeta_{\mathrm{A}}r)$ with normalization constants $N_{n_{\mathrm{A}}}$, orbital coefficients ζ_{A}, and primary quantum numbers $n_{\mathrm{H}} = 1$ and $n_{\mathrm{F}} = 2$. For VB/GCE I and CE calculations, the iterative procedure for the H atom in ref 2 is preserved. Figure 1 shows the F atom charge in $\mathrm{HF}_{(g)}$ as a function of the bond distance R_{HF} predicted by two quantum methods: the electrostatic potential (ESP) fitting[23−25] and the Mulliken[21,22] charges from generalized valence-bond (1/2)[36] [GVB(1/2)]/6-31G** calculations, and by three classical methods: Goddard-Rappé CE, eq 7, and VB/GCE I and II

TABLE 1: Parameters for Two Implementations of the Valence-Bond Generalized Charge Equilibration (VB/GCE) Model: VB/GCE I and II

	VB/GCE I Parameters[a]			VB/GCE II Parameters[b]		
atom	$\chi_{\mathrm{A}}{}^{0}$ (eV)	$\eta_{\mathrm{A}}{}^{0}$ (eV)	ζ_{A} (a.u.)	$\chi_{\mathrm{A}}{}^{0}$ (eV)	$\eta_{\mathrm{A}}{}^{0}$ (eV)	ζ_{A} (a.u.)
F	10.874	7.474	0.9206	10.41	eq 18	0.9206
H	4.528	6.9452	1.0698	7.180	7.49	1.6020

[a] Ref 2. [b] Ref 14.

($\bar{Q}_{\mathrm{F}}$), eq 36, charges. Figure 2 shows the same as Figure 1 but for VB/GCE I and II, their VB Model 3 Mulliken charges $\bar{Q}_{\mathrm{F}}^{(\mathrm{Mull})}$, eq 35, are plotted instead. The GVB(1/2)/6-31G** calculations were performed with the program *Jaguar* 4.2 (*Jaguar* 4.2, Schrödinger, Inc., Portland, Oregon, 2000). It is well-known that there are different ways to calculate charges in ab initio methods (via ESP, Mulliken, Löwdin, Coulson, etc., analyses) and those charges often disagree considerably with one another. For that reason, only two relevant types of charge (ESP and Mulliken) are used in these tests since it would be impossible to match a given VB/GCE or CE charge under a particular parametrization with all the greatly differing ab initio charges (ESP, Mulliken, Löwdin, Coulson, etc.) in a larger set. The ESP fitting charges are specially selected for these tests because those charges aim at reproducing the electrostatic potential of a molecule; that direct electrostatic definition of the ESP charges is comparable to the electrostatic description of the VB/GCE and CE models; the present ESP fitting level matches the total charge and dipole moment of $\mathrm{HF}_{(\mathrm{g})}$. The ab initio Mulliken charges are also used because that type of charge arise in the theoretical definition of the VB/GCE and CE charges; in fact, the provided parametrizations try to make the Mulliken-related VB/GCE and CE charges be as close as possible to the ESP ones. Other types of charges (Löwdin, Coulson, etc.) do not have a direct physical (like ESP) or theoretical (like Mulliken) connection with the VB/GCE and CE models and are therefore less significant in these preliminary tests; those additional charges will be tested in a future publication. Previous CE publications[13,27] considered similar number and types of charges as the ones used here. Inspection of Figures 1 and 2 reveals that the CE model satisfactorily predicts the F atom charge around the $\mathrm{HF}_{(\mathrm{g})}$ equilibrium bond distance [$\bar{Q}_{\mathrm{F}} = 0.462$ (CE[2]), 0.415 (experimental[37]), at $R_{\mathrm{Eq.\ HF}} = 0.9171$ Å[38]) but fails at dissociation; contrastingly, all of the other methods behave acceptably at dissociation. The VB/GCE I and II original and Mulliken charges agree satisfactorily with the GVB(1/2)/6-31G** ESP fitting charges over all separations R_{HF}, with the VB/GCE I Mulliken charges exhibiting the best agreement. Equation 36 was also obtained from the hypothesized PE-CC-QVB2 model[27] and tested in the dissociations of $\mathrm{LiH}_{(\mathrm{g})}$[27] and $\mathrm{NaCl}_{(\mathrm{g})}$.[28] In both cases, eq 36 also provided satisfactory charge predictions at dissociation when compared with the Mulliken charges at the GVB(1/2)/6-31G ($\mathrm{LiH}_{(\mathrm{g})}$) and the complete active space (CAS)/3-21G levels ($\mathrm{NaCl}_{(\mathrm{g})}$). All of those tests demonstrate the adequacy of the derived VB/GCE model to predict atomic charges. Tests with other diatomic molecules, and involving additional ab initio charges and other properties, will be presented in a future publication.

C. Additional VB/GCE Models for Neutral Diatomic Molecules. Approximations I−VII on VB Model 3 lead to the VB/GCE model for neutral diatomic molecules. However, it is instructive to consider some modifications in the above approximations to obtain additional VB/GCE models. A critical step in the previous derivations is the map in Approximation I that reduces the two independent VB coefficients to only one independent variable (q_{AB}). Obviously, various 2-to-1 maps of that kind can be devised but the following four prove fruitful in subsequent discussions:

$$\text{Map 2−:}\quad c_2^{(3)} = -c_3^{(3)} = \frac{q_{\mathrm{AB}}}{\sqrt{2}};\ c_1^{(3)} = \sqrt{1 - q_{\mathrm{AB}}^2};$$

$$\text{Map 2′−:}\quad c_2^{(3)} = -c_3^{(3)} = \sqrt{\frac{1 - q_{\mathrm{AB}}^2}{2}};\ c_1^{(3)} = q_{\mathrm{AB}};$$

$$\text{Map 2+:}\quad c_2^{(3)} = c_3^{(3)} = \frac{q_{\mathrm{AB}}}{\sqrt{2}};\ c_1^{(3)} = \sqrt{1 - q_{\mathrm{AB}}^2};$$

$$\text{Map 2′+:}\quad c_2^{(3)} = c_3^{(3)} = \sqrt{\frac{1 - q_{\mathrm{AB}}^2}{2}};\ c_1^{(3)} = q_{\mathrm{AB}} \tag{37}$$

where the $c_1{}^{(3)}(q_{\mathrm{AB}})$ are obtained via the normalization condition under Approximation II; Map 2− is the same as that in Approximation I. By applying each of the above maps along with Approximations II−VII to the VB Model 3 energy, four different VB/GCE energy expressions are obtained:

$$E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)}(Q_{\mathrm{A}}) = A^{\mathrm{VB/GCE}} + B^{\mathrm{VB/GCE}} Q_{\mathrm{A}} + C^{\mathrm{VB/GCE}} Q_{\mathrm{A}}{}^2;$$

$$E_{AB}^{\mathrm{VB/GCE}(2'-)}(Q_{\mathrm{A}}) = A^{\mathrm{VB/GCE}} + B^{\mathrm{VB/GCE}} Q_{\mathrm{A}} + C^{\mathrm{VB/GCE}} (1 - Q_{\mathrm{A}}{}^2);$$

$$E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2+)}(Q_{\mathrm{A}}) = A^{\mathrm{VB/GCE}} + \tilde{B}^{\mathrm{VB/GCE}} Q_{\mathrm{A}} + C^{\mathrm{VB/GCE}} Q_{\mathrm{A}}{}^2;$$

$$E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2'+)}(Q_{\mathrm{A}}) = A^{\mathrm{VB/GCE}} + \tilde{B}^{\mathrm{VB/GCE}} Q_{\mathrm{A}} + C^{\mathrm{VB/GCE}} (1 - Q_{\mathrm{A}}{}^2) \tag{38}$$

where the new coefficient $\tilde{B}^{\mathrm{VB/GCE}}$ is as follows:

$$\tilde{B}^{\mathrm{VB/GCE}} = -2(\tilde{\chi}_{\mathrm{A}}^{*} + \tilde{\chi}_{\mathrm{B}}^{*})\bar{S}_{\mathrm{AB}};\ \tilde{\chi}_{\mathrm{A/B}}^{*} = \chi_{\mathrm{A/B}}^{0} + \frac{\eta_{\mathrm{A/B}}^{0}}{2} - \int \left[\hat{V}_{\mathrm{B/A}}(\mathbf{r}_1) + \int \frac{\rho_{\mathrm{B}}(\mathbf{r}_2)d\mathbf{r}_2}{4r_{12}}\right] f_{\mathrm{A/B}}(\mathbf{r}_1)d\mathbf{r}_1 - \frac{1}{2R} \tag{39}$$

$\tilde{\chi}_{\mathrm{A/B}}^{*}$ can be formally interpreted as an unconventional perturbed electronegativity in analogy with $\chi_{\mathrm{A/B}}^{*}$ in $B^{\mathrm{VB/GCE}}$. $E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)}(Q_{\mathrm{A}})$ is identical to $E_{\mathrm{AB}}^{\mathrm{VB/GCE}}(Q_{\mathrm{A}})$, eq 32, and is the only model in eq 38 that contains the CE model as a subcase. A similar treatment to the charges renders

$$Q_{\mathrm{A}}^{(\mathrm{Mull})} = Q_{\mathrm{A}}\bar{S}_{\mathrm{AB}}\ \text{(Maps 2− and 2′−)};$$

$$Q_{\mathrm{A}}^{(\mathrm{Mull})} = -2Q_{\mathrm{A}}\bar{S}_{\mathrm{AB}}\ \text{(Maps 2+ and 2′+)} \tag{40}$$

where the relationship between $Q_{\mathrm{A}}^{(\mathrm{Mull})}$ and Q_{A} with Maps 2− and 2′− is identical to that of the previous VB/GCE model, eq 35. The optimization of the above energies ($dE_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)}(Q_{\mathrm{A}})/dQ_{\mathrm{A}} = 0$, etc.) provides the optimal charges:

$$\bar{\mathrm{Q}}_{\mathrm{A}}^{(2-)} = -\bar{\mathrm{Q}}_{\mathrm{A}}^{(2'-)} = -\frac{B^{\mathrm{VB/GCE}}}{2C^{\mathrm{VB/GCE}}};$$

$$\bar{\mathrm{Q}}_{\mathrm{A}}^{(2+)} = -\bar{\mathrm{Q}}_{\mathrm{A}}^{(2'+)} = -\frac{\tilde{B}^{\mathrm{VB/GCE}}}{2C^{\mathrm{VB/GCE}}} \tag{41}$$

whose corresponding optimal energies [$\bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)} = E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)}(\bar{Q}_{\mathrm{A}})$ etc.] are

$$\bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)} = A^{\mathrm{VB/GCE}} - \frac{B^{\mathrm{VB/GCE}\ 2}}{4C^{\mathrm{VB/GCE}}};$$

$$\bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2'-)} = A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}} + \frac{B^{\mathrm{VB/GCE}\ 2}}{4C^{\mathrm{VB/GCE}}};$$

$$\bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2+)} = A^{\mathrm{VB/GCE}} - \frac{\tilde{B}^{\mathrm{VB/GCE}\ 2}}{4C^{\mathrm{VB/GCE}}};$$

$$\bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2'+)} = A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}} + \frac{\tilde{B}^{\mathrm{VB/GCE}\ 2}}{4C^{\mathrm{VB/GCE}}} \tag{42}$$

Maps 2+ and 2′+ bring about some curious features in their corresponding energy and charge expressions. For instance, unlike B^{CE} and $B^{\mathrm{VB/GCE}}$, $\tilde{B}^{\mathrm{VB/GCE}}$ does not contain an electronegativity difference $\tilde{\chi}_{\mathrm{A}}^{*} - \tilde{\chi}_{\mathrm{B}}^{*}$ but a sum $\tilde{\chi}_{\mathrm{A}}^{*} + \tilde{\chi}_{\mathrm{B}}^{*}$, a term that impedes describing charge transfers as driven by electronegativiy differences. Moreover, the unconventional perturbed electronegativity $\tilde{\chi}_{\mathrm{A/B}}^{*}$, eq 39, contains unusual environment-perturbing terms and even a hardness term: $(1/2)\eta_{\mathrm{A/B}}^{0}$; the latter's presence in $\tilde{\chi}_{\mathrm{A/B}}^{*}$ prevents the traditional separation of electronegativities and hardnesses into the linear and quadratic coefficients of the energy, respectively. Finally, the relationship between $Q_{\mathrm{A}}^{(\mathrm{Mull})}$ and Q_{A} with Maps 2+ and 2′+, eq 40, is less intuitive than that with Maps 2− and 2′− due to the −2 factor; however, that odd negative sign can be avoided by redefining $Q'_{\mathrm{A}} = -Q_{\mathrm{A}}$ so that $Q_{\mathrm{A}}^{(\mathrm{Mull})} = 2Q'_{\mathrm{A}}\bar{S}_{\mathrm{AB}}$, and by introducing $\tilde{B}^{\mathrm{VB/GCE}'} = -\tilde{B}^{\mathrm{VB/GCE}}$ so that $E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2\pm)}(Q'_{\mathrm{A}})$ remains analogous to $E_{\mathrm{AB}}^{\mathrm{VB/GCE}(2\pm)}\,(Q_{\mathrm{A}})$. The previous analysis demonstrates that even a slight modification in Approximation I can lead to unconventional VB/GCE models. All those models are further analyzed in the next section.

D. Relationship between the VB/GCE Models and the Original VB Models. The CE model deals directly with energy and charge descriptions while circumventing the use of wave functions; consequently, the VB/GCE energy and charge expressions have received most of the attention thus far. However, it is time to investigate more closely the relationship between those VB/GCE expressions and their implicit VB wave functions. In that context, it is important to determine how the VB/GCE procedure, energies and charges relate to the variational procedure, energies and charges of their original VB model. Starting with the VB Model 3 wave function $\Psi_{\mathrm{VB}}^{(3)}$, eq 13, Maps 2− and 2′− (2+ and 2′+), eq 37, impose the constraint: $c_2^{(3)} = -\,c_3^{(3)}$ ($c_2^{(3)} = c_3^{(3)}$) on the VB coefficients and thus contracts a three-state VB wave function $\Psi_{\mathrm{VB}}^{(3)}$, into a two-state VB wave function $\Psi_{\mathrm{VB}}^{(2-)}$ ($\Psi_{\mathrm{VB}}^{(2+)}$) of the VB Model 2− (2+), eq 24,

$$\begin{aligned}\Psi_{\mathrm{VB}}^{(3)} &= c_1^{(3)}\Psi_1^{(3)} + c_2^{(3)}\Psi_2^{(3)} + c_3^{(3)}\Psi_3^{(3)}\\ &= \Psi_{\mathrm{VB}}^{(2-)} = c_1^{(2-)}\Psi_1^{(2-)} + c_2^{(2-)}\Psi_2^{(2-)} \text{ (Maps } 2- \text{ and } 2'-)\\ &= \Psi_{\mathrm{VB}}^{(2+)} = c_1^{(2+)}\Psi_1^{(2+)} + c_2^{(2+)}\Psi_2^{(2+)} \text{ (Maps } 2+ \text{ and } 2'+)\end{aligned} \tag{43}$$

where

$$\begin{aligned}&c_1^{(2-)} = c_1^{(2+)} = c_1^{(3)};\; c_2^{(2-)} = \sqrt{2(1 - S_{\mathrm{AB}}{}^2)}\,c_2^{(3)};\\ &c_2^{(2+)} = \sqrt{2(1 + S_{\mathrm{AB}}{}^2)}\end{aligned} \tag{44}$$

The constraint of Maps 2− and 2′− (2+ and 2′+) also changes the VB Model 3 energy $E_{\mathrm{VB}}^{(3)}$, eq 14, into the VB Model 2− (2+) energy $E_{\mathrm{VB}}^{(2-)}$ ($E_{\mathrm{VB}}^{(2+)}$)

$$E_{\mathrm{VB}}^{(2\pm)} = c_1^{(2\pm)2}H_{11}^{(2\pm)} + c_2^{(2\pm)2}H_{22}^{(2\pm)} + 2c_1^{(2\pm)}c_2^{(2\pm)}H_{12}^{(2\pm)} \tag{45}$$

whose matrix elements under Approximations II−VII are as follows:

$$\begin{aligned}&H_{11}^{(2\pm)} = H_{11}^{(3)} = A^{\mathrm{VB/GCE}};\\ &H_{22}^{(2\pm)} = \frac{1}{2}(H_{22}^{(3)} + H_{33}^{(3)}) = A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}};\\ &H_{12}^{(2\pm)} = \frac{H_{12}^{(3)} \pm H_{13}^{(3)}}{\sqrt{2}};\; H_{12}^{(2-)} = \frac{B^{\mathrm{VB/GCE}}}{2};\; H_{12}^{(2+)} = \frac{\tilde{B}^{\mathrm{VB/GCE}}}{2}\end{aligned} \tag{46}$$

Similarly, the normalization condition of $\Psi_{\mathrm{VB}}^{(2-)}$ ($\Psi_{\mathrm{VB}}^{(2+)}$) with Approximation II is [cf. eq 25]

$$c_1^{(2\pm)2} + c_2^{(2\pm)2} = 1;\; S_{11}^{(2\pm)} = S_{22}^{(2\pm)} = 1;\; S_{12}^{(2\pm)} = 0 \tag{47}$$

The coefficients $c_1^{(2\pm)}$ and $c_2^{(2\pm)}$ can be expressed in terms of the VB/GCE charge Q_{A} via eqs 31, 37, and 44:

$$\begin{aligned}&\text{Map } 2- \text{ and } 2+:\; c_1^{(2\pm)} = \sqrt{1 - Q_{\mathrm{A}}^2};\\ &\qquad c_2^{(2\pm)} = Q_{\mathrm{A}} \text{ (Approx. II−VII)}\\ &\text{Map } 2'- \text{ and } 2'+:\; c_1^{(2\pm)} = Q_{\mathrm{A}};\\ &\qquad c_2^{(2\pm)} = \sqrt{1 - Q_{\mathrm{A}}^2} \text{ (Approx. II−VII)}\end{aligned} \tag{48}$$

The optimal coefficients $c_1^{(2\pm)}$ and $c_2^{(2\pm)}$ and energies $E_{\mathrm{VB}}^{(2\pm)}$ of the VB Models 2± are naturally obtained from their VB eigenvector equations that under Approximations I−VII are as follows:

$$\begin{pmatrix} H_{11}^{(2\pm)} - E_i^{(2\pm)} & H_{12}^{(2\pm)} \\ H_{12}^{(2\pm)} & H_{22}^{(2\pm)} - E_i^{(2\pm)} \end{pmatrix}\begin{pmatrix} c_{1i}^{(2\pm)} \\ c_{2i}^{(2\pm)} \end{pmatrix} = 0 \tag{49}$$

each having two energy eigenvalues $E_{1/2}^{(2\pm)} = E_{\mathrm{VB}\pm}^{(2\pm)}$

$$E_{\mathrm{VB}\pm}^{(2\pm)} = \frac{(H_{11}^{(2\pm)} + H_{22}^{(2\pm)})}{2} \pm \frac{(H_{11}^{(2\pm)} - H_{22}^{(2\pm)})}{2}\sqrt{1 + \frac{4H_{12}^{(2\pm)2}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})^2}} \tag{50}$$

where $H_{22}^{(2\pm)} - H_{11}^{(2\pm)} = C^{\mathrm{VB/GCE}} > 0$; notice that the ± subscript of the two eigenvalues $E_{\mathrm{VB}\pm}^{(2\pm)}$ correlates with the ± of the sum above; the (±2) superscripts only denote the VB Models 2±. From eq 46, it can be proven that $|H_{12}^{(2\pm)}| \ll |H_{22}^{(2\pm)} - H_{11}^{(2\pm)}|$; under that condition, the eigenvalues $E_{\mathrm{VB}\pm}^{(2\pm)}$ in eq 50 are ($E_{\mathrm{VB}+}^{(2\pm)} < E_{\mathrm{VB}-}^{(2\pm)}$)

$$\begin{aligned}&E_{\mathrm{VB}+}^{(2\pm)} = H_{11}^{(2\pm)} - \frac{H_{12}^{(2\pm)2}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})};\text{ (ground state)}\\ &E_{\mathrm{VB}-}^{(2\pm)} = H_{22}^{(2\pm)} + \frac{H_{12}^{(2\pm)2}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})}\text{ (excited state)}\end{aligned} \tag{51}$$

By expressing the VB matrix elements in eq 51 in terms of the VB/GCE coefficients: $A^{\mathrm{VB/GCE}}$, $B^{\mathrm{VB/GCE}}$, $\tilde{B}^{\mathrm{VB/GCE}}$, and $C^{\mathrm{VB/GCE}}$, eq 46, the eigenvalues $E_{\mathrm{VB}+}^{(2\pm)}$ are $E_{\mathrm{VB}-}^{(2\pm)}$ turn out to be identical to the VB/CGE optimal energies in eq 42

$$\begin{aligned}&E_{\mathrm{VB}+}^{(2-)} = A^{\mathrm{VB/GCE}} - \frac{B^{\mathrm{VB/GCE}\,2}}{4C^{\mathrm{VB/GCE}}} = \bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2-)};\\ &E_{\mathrm{VB}-}^{(2-)} = A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}} + \frac{B^{\mathrm{VB/GCE}\,2}}{4C^{\mathrm{VB/GCE}}} = \bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2'-)};\\ &E_{\mathrm{VB}+}^{(2+)} = A^{\mathrm{VB/GCE}} - \frac{\tilde{B}^{\mathrm{VB/GCE}\,2}}{4C^{\mathrm{VB/GCE}}} = \bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2+)};\\ &E_{\mathrm{VB}-}^{(2+)} = A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}} + \frac{\tilde{B}^{\mathrm{VB/GCE}\,2}}{4C^{\mathrm{VB/GCE}}} = \bar{E}_{\mathrm{AB}}^{\mathrm{VB/GCE}(2'+)}\end{aligned} \tag{52}$$

Similarly, the eigenvectors in eq 49 with $|H_{12}^{(2\pm)}| \ll |H_{22}^{(2\pm)} - H_{11}^{(2\pm)}|$ are as follows:

$$c_{1+}^{(2\pm)} = \sqrt{1 - c_{2+}^{(2\pm)2}}; \text{ (ground state)}$$
$$c_{2+}^{(2\pm)} = -\frac{H_{12}^{(2\pm)}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})}; \text{ (ground state)}$$
$$c_{1-}^{(2\pm)} = +\frac{H_{12}^{(2\pm)}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})}; \text{ (excited state)}$$
$$c_{2-}^{(2\pm)} = \sqrt{1 - c_{1-}^{(2\pm)2}} \text{ (excited state)} \tag{53}$$

The optimal VB charges can be obtained from the above VB coefficients via eq 48

$$\bar{Q}_{A+}^{(2\pm)}(\text{ground state}) = -\bar{Q}_{A-}^{(2\pm)}(\text{excited state}) = -\frac{H_{12}^{(2\pm)}}{(H_{22}^{(2\pm)} - H_{11}^{(2\pm)})} \tag{54}$$

By expressing the VB matrix elements in eq 54 in terms of the VB/GCE coefficients, eq 46, the VB charges $\bar{Q}_{A+}^{(2\pm)}$ and $\bar{Q}_{A-}^{(2\pm)}$ turn out to be identical to the VB/CGE optimal energies in eq 41

$$\bar{Q}_{A+}^{(2-)} \text{ (ground state)} = -\bar{Q}_{A-}^{(2-)} \text{ (excited state)} = -\frac{B^{\text{VB/GCE}}}{2C^{\text{VB/GCE}}};$$
$$\bar{Q}_{A+}^{(2+)} \text{ (ground state)} = -\bar{Q}_{A-}^{(2+)} \text{ (excited state)} = -\frac{\tilde{B}^{\text{VB/GCE}}}{2C^{\text{VB/GCE}}} \tag{55}$$

The results in eqs 52−55 demonstrate the equivalence between the VB/GCE models and their underlying VB Models 2± under Approximations I−VII, including the equivalence between the VB/GCE energy and charge optimizations and the VB Model 2± eigenvalue/eigenvector procedures under the same approximations.

The previous analysis elucidates some additional details of the VB/GCE 2− to 2′+ and CE models in relation to their parent VB models. Despite their outwardly classical appearance, the VB/GCE 2− to 2′+ and CE models certainly involve the wave functions $\Psi_{\text{VB}}{}^{(2-)}$ and $\Psi_{\text{VB}}^{(2+)}$ that nonetheless remain implicit during the VB/GCE energy and charge optimization procedures. The VB/GCE 2− and 2′− (2+ and 2′+) models involve the two-state VB wave function $\Psi_{\text{VB}}^{(2-)}$ ($\Psi_{\text{VB}}^{(2+)}$) that through either the VB/GCE or the VB procedures provides the optimal energies: $E_{\text{VB}+}^{(2-)} < E_{\text{VB}-}^{(2-)}$ ($E_{\text{VB}+}^{(2+)} < E_{\text{VB}-}^{(2+)}$), which are the energies of the ground and first-excited states of the model, and the optimal charges: $\bar{Q}_{A+}^{(2-)} = -\bar{Q}_{A-}^{(2-)}$ ($\bar{Q}_{A+}^{(2+)} = -\bar{Q}_{A-}^{(2+)}$), eqs 54−55, which are the charges of the ground and first-excited states. Equations 43, 48, and 55 show that the VB/GCE 2− and 2′− (2+ and 2′+) models predict dissociations into uncharged fragments, $\bar{Q}_{A+}^{(2\pm)} = \bar{Q}_{A-}^{(2\pm)} = 0$ in terms of the asymptotic ground $\Psi_1^{(2\pm)} = \Psi_1^{(3)}$ and first-excited $\Psi_2^{(2-)}$ ($\Psi_2^{(2+)}$) states, eq 24. That result is acceptable for model ground states (and coincides with the VB Model 3 prediction in Section 2.A), but it is less acceptable for excited states because it describes them with the nongenuine VB wave function $\Psi_2^{(2-)}$ ($\Psi_2^{(2+)}$), eq 24, instead of the genuine ones $\Psi_2^{(3)}$ (Ionic I A^+ B^-) and $\Psi_3^{(3)}$ (Ionic II A^- B^+), eq 12. That situation and the fact that the excited-state charges are the negative of their ground-state counterparts indicate that the excited-state description by the VB Model 2− (2+) is less satisfactory. Nevertheless, the VB/GCE 2− model implies the wave function $\Psi_{\text{VB}}^{(2-)}$ that corresponds to the ground-state of the model molecule AB and that leads to a satisfactory description of the molecule dissociation into neutral species, $\bar{Q}_{A+}^{(2-)} = 0$, in terms of an acceptable asymptotic ground state: $\Psi_1^{(2-)} = \Psi_1^{(3)}$. The traditional CE model, as a subcase of the previous model, also implies the wave function $\Psi_{\text{VB}}^{(2-)}$ but can no longer provide a correct dissociation description due to the restriction imposed on the atomic overlap by Approximation IX.

Conclusions

The present work, Paper I, develops the VB part of a new VB/CS approach to the CE model, whereas the next, Paper II, will develop the corresponding CS part. The main result in this work is the rigorous derivation of a classical VB/GCE model for neutral diatomic molecules from a quantum VB model; that VB/GCE model contains the traditional CE model as a subcase. The VB/GCE model exhibits some improvements over its CE counterpart, the most important being its satisfactory description of charge-transfer processes at dissociation as illustrated with $HF_{(g)}$ $LiH_{(g)}$ and $NaCl_{(g)}$ (Section 2.B). The VB/GCE model derivation starts with the two-electron, three-state, VB Model 3 defined by five rules (Rules I−V; Section 2.A). The VB/GCE model is obtained from the VB Model 3 by sequentially applying to the latter seven approximations (Approximations I−VII; Section 2.B), whereas the traditional CE model is obtained from the VB/GCE model by applying two additional approximations (Approximations VIII and IX; Section 2.B). The previous procedure establishes a Q/C connection between the quantum-mechanical description of the VB Model 3 and the classical-electrostatics description of the VB/GCE and CE models. Through that Q/C connection, the CE charges and the CE modulating factor J_{AB}^{CE} in the Coulomb interactions are finally elucidated in terms of the VB Model 3 Mulliken charges and the atomic interactions, respectively. By generalizing the VB coefficients map in Approximation I into the Maps 2−, 2′−, 2+, and 2′+, the additional VB/GCE 2− to 2′+ models are obtained (Section 2.C), where the VB/GCE 2− model is identical to the previous VB/GCE model containing the CE subcase. Some of the additional models (e.g., VB/GCE 2+ and 2′+) exhibit unconventional features, particularly in the energy coefficients traditionally associated with the electronegativity. An analysis of the VB/GCE 2− to 2′+ and CE models (Section 2.D) proves that despite their classical appearance, those models involve two-state VB wave functions, and that their VB/GCE optimization procedures are equivalent to the VB eigenvector equations of their underlying VB models (i.e., the VB Models 2− and 2+). The VB/GCE 2− to 2′+ models predict optimal charges for both the ground and excited states of their corresponding VB models, although the excited-state descriptions seem less satisfactory. The VB/GCE 2− model and its CE subcase imply a two-state VB wave function and a charge description that correspond to the ground state. The presented VB part of a VB/CS approach to the CE mode dealt with neutral diatomic molecules, but it is not restricted to those types of systems. In fact, the VB/CS treatment of cases involving polyatomic molecules will be presented in later papers in this series. The Q/C connection found between the quantum-mechanical description of the VB models and the classical-electrostatics description of the VB/GCE and CE models will be further elaborated with the quasi-classical[30−32] VB CS sets to be introduced in Paper II. Paper II will be submitted for publication soon.

Appendix

Derivation of the VB/GCE Energy and Charges. The VB/GCE energy $E_{AB}^{\text{VB/GCE}}$, eqs 32−34 is obtained from the VB Model

3 energy $E_{\mathrm{VB}}^{(3)}$, eq 14, via Approximations I−VII as follows. First, Approximations I and II change the VB Model 3 normalization condition, eq 14, into

$$1 = c_1^2(q_{\mathrm{AB}}) + c_2^2(q_{\mathrm{AB}}) + c_3^2(q_{\mathrm{AB}}) = c_1^2(q_{\mathrm{AB}}) + q_{\mathrm{AB}}{}^2;$$
$$c_1(q_{\mathrm{AB}}) = \sqrt{1 - q_{\mathrm{AB}}{}^2} \text{ (Approx. I and II)} \qquad \text{(A1)}$$

from which $c_1(q_{\mathrm{AB}})$ is obtained. $E_{\mathrm{VB}}^{(3)}$, eq 14, can be split into diagonal $E_{\mathrm{VB}}^{\mathrm{On}}$ and off-diagonal $E_{\mathrm{VB}}^{\mathrm{Off}}$ parts that collect the diagonal and off-diagonal VB energy matrix elements, respectively:

$$E_{\mathrm{VB}}^{(3)}(c_1^{(3)}, c_2^{(3)}, c_3^{(3)}) = E_{\mathrm{VB}}^{\mathrm{On}} + E_{\mathrm{VB}}^{\mathrm{Off}};$$
$$E_{\mathrm{VB}}^{\mathrm{On}}(c_1^{(3)}, c_2^{(3)}, c_3^{(3)}) = c_1^{(3)2}H_{11}^{(3)} + c_2^{(3)2}H_{22}^{(3)} + c_3^{(3)2}H_{22}^{(3)};$$
$$E_{\mathrm{VB}}^{\mathrm{Off}}(c_1^{(3)}, c_2^{(3)}, c_3^{(3)}) = 2c_1^{(3)}c_2^{(3)}H_{12}^{(3)} + 2c_1^{(3)}c_3^{(3)}H_{13}^{(3)} + 2c_2^{(3)}c_3^{(3)}H_{23}^{(3)} \qquad \text{(A2)}$$

with the map in Approximation I, $E_{\mathrm{VB}}^{\mathrm{On}}$ and $E_{\mathrm{VB}}^{\mathrm{Off}}$ become

$$E_{\mathrm{VB}}^{\mathrm{On}}(q_{\mathrm{AB}}) = c_1^{(3)2}(q_{\mathrm{AB}})H_{11}^{(3)} + \frac{q_{\mathrm{AB}}{}^2}{2}(H_{22}^{(3)} + H_{33}^{(3)});$$
$$E_{\mathrm{VB}}^{\mathrm{Off}}(q_{\mathrm{AB}}) = 2c_1^{(3)}(q_{\mathrm{AB}})\frac{q_{\mathrm{AB}}}{\sqrt{2}}(H_{12}^{(3)} - H_{13}^{(3)}) + q_{\mathrm{AB}}{}^2H_{23}^{(3)} \text{ (Approx. I)} \qquad \text{(A3)}$$

Then, Approximations III−V change $F_{11}^{(3)}(R)$, $H_{11}^{(3)}$, $H_{12}^{(3)}$, $H_{13}^{(3)}$, and $H_{23}^{(3)}$ into

$$F_{11}^{(3)}(R) = J_{\mathrm{AB}} + V_{\mathrm{AA}}^{B} + V_{BB}^{A} + \frac{1}{R};$$
$$H_{11}^{(3)} = E_A^0 + E_B^0 + F_{11}^{(3)}(R);$$
$$H_{23}^{(3)} = 0;$$
$$H_{12}^{(3)} = \frac{1}{2\sqrt{2}}\left(h_{AA} + 3h_{\mathrm{BB}} + V_{\mathrm{AA}}^{\mathrm{B}} + 3V_{\mathrm{BB}}^{\mathrm{A}} + J_{\mathrm{BB}} + J_{\mathrm{AB}} + \frac{2}{R}\right)\bar{S}_{\mathrm{AB}};$$
$$H_{13}^{(3)} = \frac{1}{2\sqrt{2}}\left(h_{\mathrm{BB}} + 3h_{\mathrm{AA}} + V_{\mathrm{BB}}^{\mathrm{A}} + 3V_{\mathrm{AA}}^{\mathrm{B}} + J_{\mathrm{AA}} + J_{\mathrm{AB}} + \frac{2}{R}\right)\bar{S}_{\mathrm{AB}} \text{ (Approx. III−V)} \qquad \text{(A4)}$$

where $Z_{\mathrm{A}}^{\mathrm{eff}} = Z_{\mathrm{B}}^{\mathrm{eff}} = +1$; $\bar{S}_{\mathrm{AB}} = S_{\mathrm{AB}}(R)/S_{\mathrm{AB}}^0$ is a generalized overlap. Approximations III−V do not change $F_{22}^{(3)}(R)$, $F_{33}^{(3)}(R)$, $H_{22}^{(3)}$, and $H_{33}^{(3)}$. With the above changes, $E_{\mathrm{VB}}^{\mathrm{On}}$ becomes

$$\begin{aligned}E_{\mathrm{VB}}^{\mathrm{On}} &= (1 - q_{\mathrm{AB}}{}^2)H_{11}^{(3)} + \frac{q_{\mathrm{AB}}{}^2}{2}(H_{22}^{(3)} + H_{33}^{(3)})\\ &= H_{11}^{(3)} + \frac{q_{\mathrm{AB}}{}^2}{2}(H_{22}^{(3)} + H_{33}^{(3)} - 2H_{11}^{(3)})\\ &= E_{\mathrm{A}}^0 + E_{\mathrm{B}}^0 + F_{11}^{(3)}(R) + [\mathrm{IP}_{\mathrm{A}} - \mathrm{EA}_{\mathrm{B}} + \mathrm{IP}_{\mathrm{B}} - \mathrm{EA}_{\mathrm{A}} +\\ &\qquad F_{22}^{(3)}(R) + F_{33}^{(3)}(R) - 2F_{11}^{(3)}(R)]\frac{q_{\mathrm{AB}}{}^2}{2}\\ &= E_{\mathrm{A}}^0 + E_{\mathrm{B}}^0 + F_{11}^{(3)}(R) + (\eta_{\mathrm{A}}^0 + \eta_{\mathrm{B}}^0 - J_{\mathrm{AB}})q_{\mathrm{AB}}{}^2\\ &= A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}}q_{\mathrm{AB}}{}^2 \text{ (Approx. I − V)}\end{aligned} \qquad \text{(A5)}$$

where

$$\frac{F_{22}^{(3)}(R) + F_{33}^{(3)}(R)}{2} - F_{11}^{(3)}(R) = -J_{\mathrm{AB}} \text{ (Approx. III−V)} \qquad \text{(A6)}$$

has been used in the last line; notice the subtle cancelation of terms in eq A6 that renders $-J_{\mathrm{AB}}$ for the CE Coulomb interaction $-J_{\mathrm{AB}}Q_{\mathrm{A}}{}^2 = J_{\mathrm{AB}}Q_{\mathrm{A}}Q_{\mathrm{B}}$ in eq A10 below. Similarly, $E_{\mathrm{VB}}^{\mathrm{Off}}$ becomes

$$\begin{aligned}E_{\mathrm{VB}}^{\mathrm{Off}} &= 2c_1(q_{\mathrm{AB}})\frac{q_{\mathrm{AB}}}{\sqrt{2}}(H_{12}^{(3)} - H_{13}^{(3)})\\ &= c_1(q_{\mathrm{AB}})\frac{q_{\mathrm{AB}}}{2}(-2h_{\mathrm{AA}} - 2V_{\mathrm{AA}}^{\mathrm{B}} - J_{\mathrm{AA}} + 2h_{\mathrm{BB}} + 2V_{\mathrm{BB}}^{\mathrm{A}} +\\ &\qquad J_{\mathrm{BB}})\bar{S}_{\mathrm{AB}}\\ &= c_1(q_{\mathrm{AB}})\frac{q_{\mathrm{AB}}}{2}(\mathrm{IP}_{\mathrm{A}} + \mathrm{EA}_{\mathrm{A}} - 2V_{\mathrm{AA}}^{\mathrm{B}} - \mathrm{IP}_{\mathrm{B}} - \mathrm{EA}_{\mathrm{B}} +\\ &\qquad 2V_{\mathrm{BB}}^{\mathrm{A}})\bar{S}_{\mathrm{AB}}\\ &= c_1(q_{\mathrm{AB}})q_{\mathrm{AB}}(\chi_{\mathrm{A}}^0 - V_{\mathrm{AA}}^{\mathrm{B}} - J_{\mathrm{AB}} - \chi_{\mathrm{B}}^0 + V_{\mathrm{BB}}^{\mathrm{A}} +\\ &\qquad J_{\mathrm{AB}})\bar{S}_{\mathrm{AB}} \text{ (Approx. I − V)}\end{aligned} \qquad \text{(A7)}$$

where the term $(J_{\mathrm{AB}} - J_{\mathrm{AB}}) = 0$ has been added in the last line. By considering the charge density $\rho_{\mathrm{A/B}}(\mathbf{r})$ and the Fukui functions[20] $f_{\mathrm{A/B}}(\mathbf{r}) \approx \rho_{\mathrm{A/B}}^{\mathrm{HOMO}}(\mathbf{r}) = \rho_{\mathrm{A/B}}(\mathbf{r}) = \phi_{\mathrm{A/B}}^2(\mathbf{r})$ of the neutral atom A/B, the integrals $V_{\mathrm{AA}}^{\mathrm{B}}$ and J_{AB}, and the perturbed electronegativity χ_{A}^* become:

$$V_{\mathrm{AA}}^{\mathrm{B}} = \langle\phi_{\mathrm{A}}|\hat{V}_{\mathrm{B}}|\phi_{\mathrm{A}}\rangle = \int \hat{V}_{\mathrm{B}}(\mathbf{r}_1)f_{\mathrm{A}}(\mathbf{r}_1)d\mathbf{r}_1;$$
$$J_{\mathrm{AB}} = \int\int \frac{\rho_{\mathrm{B/A}}(\mathbf{r}_2)}{r_{12}}f_{\mathrm{A/B}}(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2;$$
$$\begin{aligned}\chi_{\mathrm{A}}^* &= \chi_{\mathrm{A}}^0 - V_{\mathrm{AA}}^{\mathrm{B}} - J_{\mathrm{AB}}\\ &= \chi_{\mathrm{A}}^0 - \int\left[\hat{V}_{\mathrm{B}}(\mathbf{r}_1) + \int \frac{\rho_{\mathrm{B}}(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2\right]f_{\mathrm{A}}(\mathbf{r}_1)d\mathbf{r}_1\end{aligned} \qquad \text{(A8)}$$

with analogous expressions for $V_{\mathrm{BB}}^{\mathrm{A}}$ and χ_{B}^*. With those last expressions, $E_{\mathrm{VB}}^{\mathrm{Off}}$, eq A7, becomes:

$$\begin{aligned}E_{\mathrm{VB}}^{\mathrm{Off}} &= c_1(q_{\mathrm{AB}})q_{\mathrm{AB}}(\chi_{\mathrm{A}}^* - \chi_{\mathrm{B}}^*)\bar{S}_{\mathrm{AB}}\\ &= c_1(q_{\mathrm{AB}})q_{\mathrm{AB}}B^{\mathrm{VB/GCE}} \text{ (Approx. I − V)}\end{aligned} \qquad \text{(A9)}$$

By adding $E_{\mathrm{VB}}^{\mathrm{On}}$, eq A5, and $E_{\mathrm{VB}}^{\mathrm{Off}}$, eq A9, into $E_{\mathrm{VB}}^{(3)} = E_{\mathrm{VB}}^{\mathrm{On}} + E_{\mathrm{VB}}^{\mathrm{Off}}$, eq A2, expanding $c_1(q_{\mathrm{AB}}) = (1 - q_{\mathrm{AB}}{}^2)^{1/2} = 1 - q_{\mathrm{AB}}{}^2/2 + ...$, eq A1, in $E_{\mathrm{VB}}^{\mathrm{Off}}$, and applying Approximations VI−VII, $E_{\mathrm{VB}}^{(3)}$ finally becomes $E_{\mathrm{VB}}^{(3)} = E_{\mathrm{AB}}^{\mathrm{VB/GCE}}(Q_{\mathrm{A}})$, where (cf. eqs 32−34),

$$\begin{aligned}E_{\mathrm{AB}}^{\mathrm{VB/GCE}}(Q_{\mathrm{A}}) &= A^{\mathrm{VB/GCE}} + C^{\mathrm{VB/GCE}}q_{\mathrm{AB}}^2 +\\ &\qquad q_{\mathrm{AB}}\left(1 - \frac{q_{\mathrm{AB}}^2}{2} + ...\right)B^{\mathrm{VB/GCE}}\\ &= A^{\mathrm{VB/GCE}} + B^{\mathrm{VB/GCE}}Q_{\mathrm{A}} + C^{\mathrm{VB/GCE}}Q_{\mathrm{A}}^2\\ &= E_{\mathrm{A}}^0 + E_{\mathrm{B}}^0 + F_{11}^{(3)} + (\chi_{\mathrm{A}}^* - \chi_{\mathrm{B}}^*)\bar{S}_{\mathrm{AB}}Q_{\mathrm{A}} +\\ &\qquad (\eta_{\mathrm{A}}^0 + \eta_{\mathrm{B}}^0 - J_{\mathrm{AB}})Q_{\mathrm{A}}^2\\ &= E_{\mathrm{A}}^0 + E_{\mathrm{B}}^0 + F_{11}^{(3)} + \chi_{\mathrm{A}}^*\bar{S}_{\mathrm{AB}}Q_{\mathrm{A}} + \chi_{\mathrm{B}}^*\bar{S}_{\mathrm{AB}}Q_{\mathrm{B}} +\\ &\qquad \eta_{\mathrm{A}}^0Q_{\mathrm{A}}^2 + \eta_{\mathrm{B}}^0Q_{\mathrm{B}}^2 + J_{\mathrm{AB}}Q_{\mathrm{A}}Q_{\mathrm{B}} \text{ (Approx. I − VII)}\end{aligned} \qquad \text{(A10)}$$

The VB/GCE charge $Q_{\mathrm{A}} = (-Q_{\mathrm{B}})$ is obtained from the VB Model 3 Mulliken charge description via Approximations I−VII in a similar way. With Approximations I−V, the VB Model 3 Mulliken number of electrons $N_{\mathrm{A}}^{(\mathrm{Mull})}$, eq 22, becomes:

$$\begin{aligned} N_{\mathrm{A}}^{(\mathrm{Mull})} &= c_1^{(3)2} + 2c_2^{(3)2} - \frac{2}{\sqrt{2}} c_1^{(3)} c_2^{(3)} \bar{S}_{\mathrm{AB}} \\ &= 1 - \frac{2}{\sqrt{2}} c_1^{(3)} c_2^{(3)} \bar{S}_{\mathrm{AB}} \\ &= 1 - q_{\mathrm{AB}} \sqrt{1 - q_{\mathrm{AB}}^2}\, \bar{S}_{\mathrm{AB}} \\ &= 1 - q_{\mathrm{AB}} \left(1 - \frac{q_{\mathrm{AB}}^2}{2} + \ldots \right) \bar{S}_{\mathrm{AB}} \text{ (Approx. I} - \text{V)} \end{aligned} \tag{A11}$$

that with Approximations VI and VII readily renders,

$$\begin{aligned} N_{\mathrm{A}}^{(\mathrm{Mull})} &= 1 - Q_{\mathrm{A}} \bar{S}_{\mathrm{AB}}; \\ Q_{\mathrm{A}}^{(\mathrm{Mull})} &= 1 - N_{\mathrm{A}} = Q_{\mathrm{A}} \bar{S}_{\mathrm{AB}} \text{ (Approx. I} - \text{VII)} \end{aligned} \tag{A12}$$

where $Q_{\mathrm{A}}^{(\mathrm{Mull})}$ is the VB Model 3 Mulliken charge, eq 22 (cf., eq 35).

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