An Empirical Charge Transfer Potential with Correct Dissociation Limits

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The empirical valence bond (EVB) method [J. Chem. Phys. 52, 1262 (1970)] has always embodied charge transfer processes. The mechanism of that behavior is examined here and recast for use as a new empirical potential energy surface for large-scale simulations. A two-state model is explored. The main features of the model are: (1) Explicit decomposition of the total system electron density is invoked; (2) The charge is defined through the density decomposition into constituent contributions; (3) The charge transfer behavior is controlled through the resonance energy matrix elements which cannot be ignored; and (4) A reference-state approach, similar in spirit to the EVB method, is used to define the resonance state energy contributions in terms of “knowable” quantities. With equal validity, the new potential energy can be expressed as a nonthermal ensemble average with a nonlinear but analytical charge dependence in the occupation number. Dissociation to neutral species for a gas-phase process is preserved. A variant of constrained search density functional theory is advocated as the preferred way to define an energy for a given charge.

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I. INTRODUCTION

Charge transfer is ubiquitous in physical processes affecting biological, chemical, and materials systems. The representation of charge transfer is of intense current interest throughout the physical sciences. A powerful concept in both modeling and understanding how charges redistribute themselves during a physical process is chemical potential equalization.\textsuperscript{1–6} To apply chemical potential equalization successfully, it is essential to use a charge-dependent energy model which behaves correctly for all configurations encountered in the process of interest.

Consider a diatomic molecule AB. Atom A is assumed to be more electropositive than atom B. We are interested in charge disproportionation reactions typified by

\[
A^0B^0 \leftrightarrow A^+B^-q \quad \text{(1)}
\]

and

\[
A_2 + B_2 \leftrightarrow 2A^+B^-q, \quad \text{(2)}
\]

where the charge \(q\) is not necessarily an integer. Charge disproportionation and transfer reactions are important in electron transfer in biophysical systems,\textsuperscript{7–9} enzyme catalysis reactions,\textsuperscript{10,11} and such processes as electron-hole production and recombination in organic semiconductors.\textsuperscript{12} For dimers (\(B = A\)), Eq. (1) corresponds to broken charge-symmetry states. Furthermore, Eqs. (1) and (2) have been the prototype reactions for a wide variety of theoretical studies of chemical bonding,\textsuperscript{3,13–20}

The most prevalent model potential for charged species is the quadratic expansion of the classical electrostatic potential,\textsuperscript{4,6,21–23}

\[
E \approx E_0(R) + E_1(R) q + 1/2 (E_2(R) - V(R)) q^2. \quad \text{(3)}
\]

The \(E_i(R)\) are expansion coefficients which are atom-type dependent and \(V(R)\) is an interionic potential representing the classical electrostatic contribution. In general all of these functions depend on the separation \(R\). The charge \(q\) is usually, but not always, independent of \(R\). \(V(R)\) approaches a \(1/R\) dependence at sufficiently large \(R\). \(E_0(R)\) contains the charge-independent short-range and dispersion interactions between the atoms. The other expansion coefficients are frequently interpreted in terms of physical quantities such as chemical potential and hardness.\textsuperscript{4,6,24–31} The quadratic form has the virtue of simplicity and works adequately when the range of \(R\) is small enough to prevent \(q\) from changing appreciably.

If Eq. (3) is used at all separations, the atoms in the AB molecule will remain ionic even at separations where they are supposed to return to neutral states. For those situations where charge transfer does occur, alternative functional forms of charge dependence need to be invoked. For instance, Alavi et al.\textsuperscript{21} and Grochowski and coworkers\textsuperscript{32} use phenomenological switching functions to effect charge transfer. At very large separations, though, it is known that the charge dependence becomes piecewise linear (Fig. 1).\textsuperscript{2,19,33}

Morales and Martínez\textsuperscript{34} (hereafter referred to as MM) conclude that the “grand canonical” (GC) approach\textsuperscript{2} cannot describe a realistic charge transfer process. In the GC approach each atom is considered to be an open sys-
The solid line corresponds to the energy of the isolated atoms as a function of acquired charge \( q \) (measured with respect to charge transfer from the cation). The dashed curve corresponds to a quadratic representation of the charge dependence. The energy minimizes at \( q = 0 \) for the piecewise linear model, but not for the quadratic model. At large separations, the piecewise linear model is correct. Traditionally the quadratic model is considered to be more correct at finite separations.

The three main difficulties in deriving a charge dependent potential are the same ones facing MM and others. First is to define the charge, second is to evaluate or eliminate the resonance energy matrix elements, and third is to define the energy for a particular value of \( q \). First, to define \( q \), we invoke a density-functional-theory (DFT) motivated atom-in-molecule (EVB) \( ^{36–38} \) pseudo-atom concept within the context of the EVB approach. We assume the availability of a practical density decomposition strategy \( ^{18,43–48} \) to define the pseudo-atom densities. The charge is defined as an average over the difference between two pseudo-atom densities. No restriction to Coulson \(^{36} \) or other definitions of charge \( ^{49,50} \) is necessary.

The dependence of the EVB wavefunction on \( q \) is then deduced, which in turn yields an energy for arbitrary \( q \), not just the optimum \( q \). Second, to evaluate resonance energy matrix elements, we retain the VB approach of MM, but use an empirical valence bond (EVB) \( ^{32,51,52} \) strategy, rather than explicitly evaluating a model Hamiltonian or using the MEVB averaging procedure of MM. Specifically, a reference energy is separated out for a fixed value of \( q \). To define the energy for an atom in the molecule, we require consistency between the EVB wavefunction energy and DFT energy for each atom. In so doing we are able to cast the energy of each atom into a form suitable for constructing empirical potential energy surfaces that could be used in simulations of larger systems. Third, the typical situation is that there are many wavefunctions and many electron densities that are consistent with a particular \( q \). To define a unique energy from among the possible choices, we adhere to constrained search density functional theory (CS-DFT) \( ^{41,53} \) rather than appealing to a maximum entropy principle.

To the best of our knowledge, the EVB method has not previously been combined with an atom-in-molecule approach. \(^{31} \) von Szentpály and coworkers define atomic charges, but their definition is implicitly limited to a quadratic dependence. \(^{27–29} \) Grochowski and coworkers \(^{32} \) use EVB parameterized by \( ab \text{ initio} \) calculations for key molecular fragments and for defining the charges. The charges are defined with a phenomenological spatial de-
pendence that does maintain correct dissociation to neutrals. Furthermore, the charge dependence of the final potential is purely electrostatic.

The inconsistency between the GC and classical electrostatic forms is explained in Cioslowski and Stefanov\textsuperscript{19} using a different definition of $q$, which is based on the total system wavefunction. The charge is expressed as a perturbation on the molecular Hamiltonian $H$. Computed atom-in-molecule equilibrium charges are used in subsequent “charge-constrained” calculations to study the energy and electronegativity dependences about the ground-state atom-in-molecule charges. Nalewajski\textsuperscript{33} provides a simplified rendition of Cioslowski and Stefanov, but only for orthogonal resonance states. While physically correct, these efforts have not been cast in the form of general purpose potential energy surfaces. In particular, neither attempts to resolve the resonance energy issue in a way that is tractable for large-scale simulations.

Here we derive a charge-dependent empirical potential which faithfully represents charge transfer as a function of separation between atom A and an entity B. In the simplest case, entity B is another atom. More generally, B represents a collective embedding environment or reservoir.\textsuperscript{2,16} The charge may be fractional. Our primary interest is in deriving a general functional form with correct physical and chemical behavior at all interaction strengths rather than providing an exact treatment of particular terms or systems. The three difficulties just outlined are addressed. We then analyze these potentials in special limiting cases and in the light of the results of Cioslowski and Stefanov\textsuperscript{19} and Nalewajski.\textsuperscript{33} Finally, we derive general models for both pair potentials and atom-in-molecule energies.

\section{THE EMPIRICAL VALENCE BOND REPRESENTATION}

The EVB method is a much more general technique than described here. Reviews of EVB are available from Warshel \textit{et al}.\textsuperscript{52} Here we confine our discussion to a 2-state model of the AB molecule. There are fixed covalent and ionic resonance states represented by wavefunctions $\psi_c$ and $\psi_i$, respectively.\textsuperscript{32,52,54,55} No assumption is made about the quality of these wavefunctions. However, $\psi_c$ retains $N_A^0$ electrons on atom A and $N_B^0$ electrons on atom B. Atoms A and B are neutral in the covalent resonance state. Consequently $N_A^0$ and $N_B^0$ are equal to their respective nuclear charges, $Z_A$ and $Z_B$. Similarly, $\psi_i$ retains $N_A^0 - 1$ electrons on atom A and $N_B^0 + 1$ electrons on atom B. In each resonance state, the total number of electrons is $N$. $\psi_c$ and $\psi_i$ are assumed to be normalized to unity. The wavefunction of the system $\psi$ is the combination\textsuperscript{36–38,56–58}

\begin{equation}
\psi = c (\psi_c + \gamma \psi_i),
\end{equation}

where $\gamma$ determines the relative ionic character. By normalization,

\begin{equation}
1/c^2 = 1 + 2 \gamma S_{ci} + \gamma^2,
\end{equation}

where

\begin{equation}
S_{ci} = \langle \psi_c | \psi_i \rangle.
\end{equation}

For the AB molecule with Hamiltonian $H$, the mixed-state energy takes the form

\begin{equation}
E = c^2 (H_{cc} + 2 \gamma H_{ci} + \gamma^2 H_{ii}),
\end{equation}

\begin{equation}
= H_{cc} + 2 \gamma H_{ci} + \gamma^2 H_{ii},
\end{equation}

where $H_{cc}$, $H_{ii}$ and $H_{ci}$ are the associated energy matrix elements.

\begin{equation}
H_{cc} = \langle \psi_c | H | \psi_c \rangle,
\end{equation}

\begin{equation}
H_{ii} = \langle \psi_i | H | \psi_i \rangle,
\end{equation}

and

\begin{equation}
H_{ci} = \langle \psi_c | H | \psi_i \rangle.
\end{equation}

Minimizing $E$ with respect to $\gamma$ gives the optimized values,

\begin{equation}
\gamma_{opt} = 1 \pm \sqrt{1 + \epsilon_{cc} \epsilon_{ii}} / \epsilon_{ii},
\end{equation}

where $\epsilon_{cc} = 2 (H_{ci} - S_{ci} H_{cc})/(H_{ii} - H_{cc})$ and $\epsilon_{ii} = 2 (H_{ci} - S_{ci} H_{ii})/(H_{ii} - H_{cc})$. The $\pm$ signs in Eq. (13) correspond to ground (gs) and excited (xs) states, whose energies are designated as $E_{gs}$ and $E_{xs}$, respectively. From Eq. (13), one can see that the off-diagonal matrix elements, $H_{ci}$ and $S_{ci}$, control charge transfer in EVB. When $S_{ci} = 0$, $\epsilon_{cc} = \epsilon_{ii} = \epsilon = 2 H_{ci}/(H_{ii} - H_{cc})$. Depending on the root, $\gamma_{opt}$ (− root) or 1/($\gamma_{opt}$ (+ root)) varies from $-1$ to $+1$. Note that as $H_{ii} - H_{cc}$ goes to zero, that is, as the covalent and ionic curves cross, charge transfer or the Coulson-Fischer transition\textsuperscript{57} becomes more abrupt. If $\psi_c$ and $\psi_i$ are nondegenerate eigenfunctions of $H$, then $H_{ci} = S_{ci} = 0$. There is either no charge transfer or there is complete charge transfer. In either case, the states do not mix.

The coefficient $\gamma$ governs the ionic contribution to $\psi$. As $\gamma$ increases, $\psi$ migrates toward more complete charge transfer. Even neglecting overlap,\textsuperscript{51,52} the ionic strength $\gamma$ interpolates between covalent and ionic states in a physically reasonable way.\textsuperscript{57} The state-to-state interpolating behavior of $\gamma$ in Eq. (13) is the essential behavior that we wish to emulate in developing a more broadly applicable charge dependent potential.

Later in the paper, two other relationships will become useful, which we provide here. First, in the spirit of EVB,\textsuperscript{52} one always wants to know the resonance energy in the terms of the ground-state $E_{gs}$, $S_{ci}$, $H_{cc}$, and $H_{ii}$. That is,

\begin{equation}
H_{ci} = E_r S_{ci} \pm \sqrt{(H_{cc} - E_r)(H_{ii} - E_r),}
\end{equation}

where
where $\tau$ is either “gs” or “xs”. The second relationship expresses $\gamma_{opt}$ as a function of these same parameters. This is done by substituting Eq. (14) into the expressions for $\epsilon_{cc}$ and $\epsilon_{ii}$. The general expression is

$$\epsilon_{\sigma\tau} = \frac{(E_{\tau} - H_{\sigma\tau})S_{\sigma} \pm \sqrt{(H_{cc} - E_{\tau})(H_{ii} - E_{\tau})}}{H_{ii} - H_{cc}} ,$$

(15)

where $\sigma\tau$ is either “cc” or “ii” and either the ground or excited state is selected.

### III. CHARGE IN THE 2-STATE EVB MODEL

We begin with the question of how to define charge in our model. There is no unique definition of the charge on an atom in a molecule. To assign charges to individual atoms, we assume that it is possible to decompose the total electron density into pseudo-atom densities. How-\[er, we do not need to specify a particular decomposi-

The total electronic energy expression analogous to Eq. (17) is

$$E = \alpha_{cc} H_{cc} + 2 \alpha_{ci} H_{ci} + \alpha_{ii} H_{ii} .$$

(18)

Eq. (18) corresponds to a non-diagonal representation of the energy. Its advantage is that the component contributions of the essential states that are thought to represent the physical system are delineated. A diagonal representation of $\Gamma$ when state mixing is important can be devised by diagonalizing $H$. For the purposes of extending the present treatment to finite temperature ensembles,2,34,35,59 this particular diagonalization of $\Gamma$ would be useful.

The $N$-electron densities of interest are $\rho$, $\rho_{cc}$, $\rho_{ci}$, and $\rho_{ii}$. They bear the usual relationships to the respective $N$-electron density matrices, $\Gamma_{\sigma\tau}$:

$$\rho_{\sigma\tau}(r) = N \int d\mathbf{r}_{N-1} \Gamma_{\sigma\tau}(\mathbf{r}_N, \mathbf{r}_N) ,$$

(19)

where $\mathbf{r}_{N-1}$ are the $3(N-1)$ dimensional spatial electronic coordinates and $\sigma\tau$ is either “cc”, “ci”, “ii”, or no subscript. $\rho$, $\rho_{cc}$, and $\rho_{ii}$ are normalized to $N$. The relationship of central interest is

$$\rho = \rho_{cc} + 2 \rho_{ci} + \rho_{ii} = \frac{\rho_{cc} + 2 \gamma_{cc} + \gamma^2 \rho_{ii}}{1 + 2 \gamma S_{cc} + \gamma^2} .$$

(20)

Recall the assumption that the covalent and ionic state wavefunctions are given and fixed. Thus the total density $\rho$ is determined solely by the value of $\gamma$.

The energies of $\rho_{cc}$ and $\rho_{ii}$ are well-defined in a conventional DFT sense.39,41 However, the “interference density”60 $\rho_{ci}$ does not have a well-defined energy in DFT. Nevertheless, its energy may be inferred from the energies of $\rho$, $\rho_{cc}$, and $\rho_{ii}$ as we will show below.

Next we assume that all of the $\rho_{\sigma\tau}$ can be decomposed into corresponding pseudo-atom densities, $\rho_{\sigma\tau, A}$ and $\rho_{\sigma\tau, B}$.60 The pseudo-atom densities $\rho_{\sigma A}$ and $\rho_{\sigma B}$ integrate to non-integer values, $N_{\sigma A}$ and $N_{\sigma B}$, whereas $\rho'^{cc, A}$, $\rho'^{cc, B}$, $\rho'^{ci, A}$, $\rho'^{ci, B}$, and $\rho'^{ii, A}$, $\rho'^{ii, B}$ are constrained to integrate to integer numbers of electrons. We use asterisks throughout to indicate atom-in-molecule quantities.

With these definitions in place, we define $q$ from either pair of total and covalent pseudo-atom densities, which others have sometimes referred to as pseudo-atom distortion densities.18,43 We choose atom A:

$$q = \int d\mathbf{r} (\rho'^{cc, A}(r) - \rho^{A}(r)))$$

$$= N_{\sigma A} - N_{\sigma A} .$$

(21)

(22)

The density decompositions must be constrained to yield the correct number of electrons prescribed by Eq. (22).61-63 Finally, we note that the present definition of $q$ falls into Truhlar’s Class II category.64,65
Now we want to eliminate $\gamma$ in favor of $q$. Assuming that a component definition of $\rho_{ci}^A(r)$ based on Eq. (20) is possible,

$$q = \frac{\gamma^2 - 2 \gamma \delta N_{ci,A}^*}{1 + 2 \gamma S_{ci} + \gamma^2},$$  \hspace{1cm} (23)$$

where

$$\delta N_{ci,A}^* \equiv \int dr \left( \rho_{ci,A}^*(r) - \left( N_{A0}/N \right) \rho_{ci}(r) \right),$$  \hspace{1cm} (24)$$

$N_{A0}$ is the number of electrons on atom A when it is in a neutral state, and the relationship $N_{ci} = \int dr \rho_{ci}(r)$ has been used. The quantity $\delta N_{ci,A}^*$ is determined by the difference between $\rho_{ci,A}^*$ and the atom A component of the decomposition of $\rho_{ci}$ with locally unbiased, electron-number decomposition.\textsuperscript{63} Clearly, different density decomposition strategies will yield somewhat different values of $\delta N_{ci,A}^*$. One possibility for determining $\delta N_{ci,A}^*$ is to require consistency with the ground-state value of $\gamma$. For instance, if $q = 0$ is optimum as for a dimer, $\gamma$ equals either 0 or 2 $\delta N_{ci,A}^*$. For Eq. (23) to be applied successfully, 2 $\delta N_{ci,A}^*$ would have to correspond to a lower energy state than $\gamma = 0$ and the value of $\gamma$ would have to be determined from a separate calculation, such as represented by Eq. (13). In such an approach, one would be effectively modeling $\delta N_{ci,A}^*$ via a correspondence with the Coulson-Fischer transition.\textsuperscript{57} Alternatively, by analogy with $\rho$, we assume that single-particle determinants (e.g. Kohn-Sham determinants\textsuperscript{46}) can be calculated for the $\rho_{ci,A}^*$\textsuperscript{47,66–68}. In a Kohn-Sham based approach, one would be effectively estimating $\rho_{ci,A}$ from the overlaps of these determinants. Additional ambiguity in $\delta N_{ci,A}^*$ arises from the choices for $\psi_c$ and $\psi_i$. These ambiguities lie behind the designation of the present approach as an empirical one. However, these ambiguities can be mitigated by using a reference state as discussed in the next Subsection. To that end, it is useful to invert Eq. (23) so that $\delta N_{ci,A}^*$ becomes a function of $q$ and $\gamma$. That relationship is

$$\delta N_{ci,A}^* = \frac{(1 - q) \gamma^2 - 2 S_{ci} \gamma - q}{2 \gamma},$$  \hspace{1cm} (25)$$

It should be understood that, in the limit that $\gamma \rightarrow 0$, $\delta N_{ci,A}^* \rightarrow 0$ also.

### B. Constructing Pair Potentials

To construct a potential energy surface for AB, one option is to use Eq. (23) to model the dependence of the charge on separation for some reference state. Some empirical potentials such as EVB and the modified embedded atom method (MEAM)\textsuperscript{69–71} utilize reference states as a model calibration method. The methods of McDonald and coworkers,\textsuperscript{21} McCammon, Grochowski, and coworkers,\textsuperscript{32} and Broughton and Mehle\textsuperscript{55} effectively make $q$ bond-length dependent. Eq. (23) provides a basis in EVB theory for their phenomenological charge transfer switching functions.

A more attractive option is to solve for $\gamma = \gamma(q)$,

$$\gamma = \frac{(\delta N_{ci,A}^* + q S_{ci}) \pm \sqrt{(\delta N_{ci,A}^* + q S_{ci})^2 + q (1 - q)}}{1 - q},$$  \hspace{1cm} (26)$$

The coefficient $\gamma$ determines the strength of the contribution of $\psi_i$ to $\psi$. Eq. (26) states how the charge governs that strength. This expression is consistent with the results of Cioslowski and Stefanov,\textsuperscript{19} which are derived from a perturbative technique. As noted previously, even if $q = 0$, $\gamma$ equals either 0 or 2 $\delta N_{ci,A}^*$. This is because the EVB model describes state mixing even when there is no charge transfer. For example, in the H$_2$ molecule, the covalent and ionic wavefunctions mix at all finite separations, but the ground state never involves charge transfer. Significantly, this formula also describes deviations from the ground-state charge.

Eq. (26) can be substituted into Eq. (9), and the variational procedure repeated. The result is the same as solving for $q$ in terms of the resonance and overlap matrix elements obtained by equating Eq. (26) and (13).

The EVB strategy is to use experimental information to eliminate the resonance energy.\textsuperscript{51,52} Here the analogous procedure is to choose a particular value of $q = q_0$ and solve for $H_{ci}$ in terms of $E(q_0)$ and the diagonal matrix elements for each $R$. (The $R$ dependence is suppressed.) The result is

$$H_{ci} = \frac{E(q_0) - \alpha_{cc}(q_0) H_{cc} - \alpha_{ii}(q_0) H_{ii}}{2 \alpha_{ci}(q_0)}.$$  \hspace{1cm} (27)$$

Substituting Eq. (27) into Eq. (18), the total energy for arbitrary $q > 0$ has the form

$$E(q) = \left( \alpha_{ci}(q)/\alpha_{ci}(q_0) \right) E(q_0) + \left( \alpha_{cc}(q) - \alpha_{cc}(q_0) \alpha_{ci}(q)/\alpha_{ci}(q_0) \right) H_{cc} + \left( \alpha_{ii}(q) - \alpha_{ii}(q_0) \alpha_{ci}(q)/\alpha_{ci}(q_0) \right) H_{ii}.$$  \hspace{1cm} (28)$$
This form might be used in lieu of classical electrostatic potentials like Eq. (3) that have been in common use. It has the structure of an ensemble average, but the coefficients of $H_{cc}$ and $H_{ii}$ are not necessarily positive semidefinite. Eq. (28) is constructed to possess the proper changes in atomic charges in the limit of molecular dissociation. The construction of a proper ensemble representation is discussed in Section 5.A.

The foundations for the quadratic dependence of the energy on charge, such as Eq. (3), must stem from Eqs. (26) and (9). However, even this simplest example of charge transfer has a considerably more complex dependence than quadratic. That dependence is clearly carried through the overlap contributions.

Once $q_0$ has been chosen, the procedure for determining a point on the potential energy surface for arbitrary values of $R$ and $q$ is as follows. From some other source(s) of information, one must have available five reference values: $E(q_0)$, its associated ionicity $\gamma_0$, $H_{cc}$, $H_{ii}$, and $S_{ci}$. For a chosen $R$, one first evaluates

(a) $\alpha_{ce}$, etc. from Eq. (17);
(b) $H_{ci}$ from Eq. (27); and
(c) $\delta N^*_{ci,A}$ from Eq. (25).

Then, for each $q$ of interest, one evaluates

(d) $\gamma(q)$ from Eq. (26) using values from Steps (a), (b), and (c); and
(e) $E(q)$ from Eq. (8).

The procedure is repeated for each value of $R$ of interest. An important question is what to choose for $q_0$. One possible choice for $q_0$ is the optimum value $q_{opt}$. However, $q_{opt}$ depends on $H_{ci}$ through Eqs. (13) and (23). This variant is equivalent to using the ground-state wavefunction as one of the basis functions in the original formulation of the problem. Eq. (28) then characterizes deviations of the energy from the ground-state energy, $E(q_{opt})$, as a function of $q$. Note that by choosing $E(q_{opt})$ to be consistent with $E(q_{opt})$, this variant and Eq. (28) will be identical.

When $q_0 = q_{opt}$, the procedure for determining a point on the potential energy surface is substantially the same as the first. Again five reference values are needed, except that knowledge of $q_{opt}$ replaces knowledge of $\gamma_0$. Relative to the first procedure, Steps (a) and (b) become to evaluate

(a) $H_{ci}$ from Eq. (14); and
(b) $\gamma_{opt}(q_{opt})$ from Eq. (13).

All of the other steps remain the same.

One can extend this model to $q$ between $-1$ and 0. The entire procedure with atom A assumed to be anionic in $\psi_i$ is repeated. In Eq. (22), for $q < 0$, one simply replaces $q$ with $-q$ and adjusts the partitioning of $\rho_{ci}$ so that atom A is anionic. Requiring continuity in the energy at $q = 0$ dictates that $-\delta N^*_{ci,A} \rightarrow \gamma(q)$ as $q \rightarrow 0^-$. Eq. (28) remains the same structurally. Equivalently, one could replace the subscript “A” with the subscript “B” everywhere in the procedure. The potential over the entire range of $q$ is then represented in a piecewise fashion. While not as rigorous as a 3-state model, the present treatment does retain substantially greater simplicity.

Another possible extension is to apply the above procedure when the two resonance states both correspond to charged species. For CaO, for example, the effective $q$ on Ca near equilibrium would be almost +2. As the CaO bond is stretched, $q$ would decrease until it passed through a region of undetermined length where it would range between +1 and 0. Then there would be one form of Eq. (28) covering the range in $q$ between 0 and +1 and a second form covering the range between +1 and +2 range.

A final extension of this model would allow the entity B to correspond to a more general environment than just one other atom. Most of the model presented here does not explicitly invoke the specific properties of a diatomic model. However, this extension requires separate considerations not pursued here.

IV. DEFINITION OF PSEUDO-ATOM ENERGIES

We now show how to define pseudo-atom energies for the 2-state model of the previous section. We do this by requiring consistency between the energies based on the density decompositions that were assumed in the previous Section and the energies that would result from the corresponding wavefunction expressions. As with $\rho$, we assume that there is a decomposition $\Gamma$ into pseudo-atom density matrices. In conformance with Rychlewski and Parr, the decomposition applies to $\Gamma$ rather than to $H$. Thus, for

$$\Gamma = \Gamma^*_A + \Gamma^*_B ,$$

the total energy decomposes into

$$E = \langle H, \Gamma^*_A \rangle + \langle H, \Gamma^*_B \rangle = E^*_A + E^*_B .$$

Analogous expressions are assumed to exist for each of the covalent and ionic contributions to the pseudo-atom energies.

The pseudo-atom densities $\rho^*_A$ and $\rho^*_B$ correspond to the pseudo-atom density matrices $\Gamma^*_A$ and $\Gamma^*_B$. In the following relations, the expressions for atoms A and B are analogous. Only the expressions for atom A will be given. We want the energies of each pseudo-atom defined via density matrices to be equal to the energies defined via densities. Consequently, we require that

$$E^*_A = E_A[\rho^*_A] .$$
This identification places a new constraint on $\Gamma_A^\ast$. Rigorously speaking, it should be optimal in the sense of Levy CS-DFT. The constraint is that $\Gamma_A^\ast$ should yield the lowest energy for all other ensemble density matrices which integrate to $\rho_A^\ast$:

$$E_A^{\text{CS-DFT}}[\rho_A^\ast] \equiv \langle H, \Gamma_A^\ast \rangle = \min_{\Gamma_A \rightarrow \rho_A^\ast} \langle H, \Gamma_A \rangle . \quad (32)$$

In terms of valence bond resonance states

$$E_A^\ast = \alpha_{cc} H_{cc,A}^\ast + 2 \alpha_{ci} H_{ci,A}^\ast + \alpha_{ii} H_{ii,A}^\ast . \quad (33)$$

Similar to $E_A^\ast$, the pure-state terms in Eqs. (33), $H_{cc,A}^\ast$ and $H_{ci,A}^\ast$, can be represented in conventional DFT language. The resonance energy cannot. Eq. (33) represents pseudo-atom energies for any $q$. To evaluate the resonance energy, we again follow the EVB strategy of determining them from some particular value of $q = q_0$. The result is

$$H_{ci,A}^\ast = \frac{E_A^\ast(q_0) - \alpha_{cc}(q_0) H_{cc,A}^\ast - \alpha_{ii}(q_0) H_{ii,A}^\ast}{2 \alpha_{ci}(q_0)} . \quad (34)$$

If $q_0$ is set equal to the optimum $q$ for each value of atomic separation, then $E(q_0) = E_A^\ast(q_0) + E_B^\ast(q_0)$ will correspond to the experimental potential energy for AB. Note that all of the energies in traditional EVB are 0 K values. Some variations of EVB incorporate temperature-dependent solvent effects. We do not include these variations here. Finite temperatures are not required to establish the model. On the other hand, there is nothing here that precludes extending the analysis to a finite temperature ensemble.\textsuperscript{2,16,33,34,59}

Substituting Eq. (34) into Eq. (33), an expression for the pseudo-atom energy is achieved. For any $q$,

$$E_A^\ast(q) = (\alpha_{ci}(q)/\alpha_{ci}(q_0)) E_A^\ast(q_0) + (\alpha_{cc}(q) - \alpha_{cc}(q_0) \alpha_{ci}(q)/\alpha_{ci}(q_0)) H_{cc,A}^\ast + (\alpha_{ii}(q) - \alpha_{ii}(q_0) \alpha_{ci}(q)/\alpha_{ci}(q_0)) H_{ii,A}^\ast . \quad (35)$$

Eq. (35) has the same structure as Eqs. (28), but refers to an individual atom. All of the quantities on the right-hand sides of these two equations can be deduced from experiment and/or decomposition calculations on resonance states and overlaps.

Using the present formulations in simulations of larger systems naturally invokes consideration of chemical potential equalization. One can obtain a statement of chemical potential equalization from Eq. (35). The total energy is given in Eq. (30). If $E$ is minimized with respect to $q$, then small deviations from $q_{opt}$ will not change the total energy to first order:

$$0 = \left. \frac{dE(q)}{dq} \right|_{q=q_{opt}} = \left. \frac{dE_A^\ast(q)}{dq} \right|_{q=q_{opt}} + \left. \frac{dE_B^\ast(-q)}{dq} \right|_{q=q_{opt}} . \quad (36)$$

or

$$\frac{dE_A^\ast(q)}{dq} \bigg|_{q=q_{opt}} = \frac{dE_B^\ast(-q)}{dq} \bigg|_{q=q_{opt}} \equiv -\mu(q) , \quad (37)$$

where $\mu$ is the chemical potential. Charge balance requires that the charges on A and B be exactly opposite. The minus sign in front of $\mu$ comes from the fact that $\mu$ is related to the negative of the change in the number of electrons on A.

V. DISCUSSION AND EXAMPLES

Here we introduce approximations consistent with the dissociation limits of AB, present a general definition of the energy for a given charge, and discuss $H_2$, HF, and LiH as examples.

A. Neglect of Differential Overlap Model

It is insightful to introduce a concept of neglect of differential overlap between resonance states, $\rho_{ci} = 0$, which we will refer to as NDOL. This leads to simple analytical expressions whose behavior can be examined in detail. NDOL is to be distinguished from zero differential overlap (ZDO),\textsuperscript{36} which refers to overlap between orbitals on different atomic centers. In the NDOL approximation, $\rho_{ci} = 0.73$. Under special conditions, ZDO implies NDOL.

In the NDOL approximation, $\delta N_{ci,A}$ and $S_{ci}$ are zero. From Eq. (26), the dependence of $\gamma$ on $q$ becomes

$$\gamma(q) = \pm \sqrt{q/(1-q)} . \quad (38)$$

From Eq. (9), the energy dependence on $q$ becomes

$$E_{\text{NDOL}}(q) = H_{cc} - 2\sqrt{q/(1-q)}|H_{ci}| + q (\text{IP}_A - \text{EA}_B) . \quad (39)$$

The $-|H_{ci}|$ construct ensures that $E_{\text{NDOL}}$ corresponds to the ground state. Here we have used the fact that, by definition of the ionization potential IP and electron affinity EA, $H_{ci} - H_{cc} = \text{IP}_A - \text{EA}_B$. These atom-in-molecule quantities include some electrostatic contributions. This quantity is also called a "bond hardness".\textsuperscript{19}

Thus, Eq. (38) is consistent with previous energy expressions obtained with Coulson charges\textsuperscript{34,36–38} and with the 2-state model of Nalewajski\textsuperscript{35}. In Coulson,\textsuperscript{36} Murrell et. al\textsuperscript{37} and McWeeny\textsuperscript{38} a fraction of ionic character is defined instead of a charge. That fraction is identical to $\gamma^2/(1 + \gamma^2)$ which is $q$ in the NDOL approximation. Clearly, at large $R$, Eq. (8) in combination with Eq. (26) approaches Eq. (39), Eq. (39) becomes linear in $q$, and $H_{ci}$, $H_{cc}$, and $H_{ci}$ approach asymptotic values (in $R$) analogous to MM’s Eq. (2.40).\textsuperscript{34} The linear behavior in the asymptotic regime is consistent with the conclusions of PPLB. Even more importantly, Eq. (39) is expressly non-analytical (i.e., it cannot be expanded in a Taylor
that Eq. (42), we achieve the ensemble representation:

\[ q_{\text{opt}}^{\text{NDOL}} = \frac{1}{2} \left( 1 - \frac{1}{\sqrt{1 + \epsilon^2}} \right), \tag{40} \]

where \( \epsilon = 2 H_{ci} / (H_{ii} - H_{cc}) \). The ground state corresponds to the negative root of \( \gamma(q) \) in Eq. (38), since as \( H_{ci} \to 0 \), \( q \) must also go to zero, assuming that \( H_{ii} - H_{cc} > 0 \). For convenience, we call the ground state value of Eq. (39) \( E_{gs}^{\text{NDOL}} = E_{gs}^{\text{NDOL}(d_{\text{opt}})} \). The solution for the resonance energy is equivalent to the well-known EVB expression\(^\text{52}\)

\[ |H_{ci}| = \sqrt{E_{gs}^{\text{NDOL}}(H_{ii} - E_{gs}^{\text{NDOL}})}. \tag{41} \]

Substituting Eq. (41) into Eq. (39), we find

\[ E_{\text{NDOL}}^{\text{NDOL}}(q) = (1 - q) H_{cc} - 2 \sqrt{(1 - q)(H_{cc} - E_{gs}^{\text{NDOL}}) q(H_{ii} - E_{gs}^{\text{NDOL}})} + q H_{ii}. \tag{42} \]

The dependence of \( E_{\text{NDOL}}^{\text{NDOL}}(q) \) on \( H_{cc} \) and \( H_{ii} \) appears to be different from that implied by Eq. (28). In fact, by setting \( E_{q_0}^{\text{NDOL}} = E_{gs}^{\text{NDOL}} \) in Eq. (28), the two expressions become identical.

We can gain further insight from Eq. (42) by solving for \( H_{cc} \) and \( H_{ii} \) in terms of \( E_{gs}^{\text{NDOL}} \approx E_{gs}, E_{ss}, \) and \( q_{\text{opt}} \approx q_{gs} \). In a typical diatomic, \( E_{ss} \) corresponds to the first electronic state which dissociates to the ions \( \text{A}^+ \) and \( \text{B}^- \). Because of the NDOL approximation, these three pieces of information are sufficient to specify the energy. To achieve the desired result, we first use the fact that \( H_{ss}^{2} \) can be derived from either eigenvalue to find that \( H_{ii} = E_{ss} + E_{cc} - H_{cc} \). Next we solve for \( H_{cc} \) from Eq. (40) assuming that we know \( q_{gs} \). The result is that

\[ H_{cc} = (1 - q_{gs}) E_{gs} + q_{gs} E_{ss}, \tag{43} \]

and

\[ H_{ii} = q_{gs} E_{gs} + (1 - q_{gs}) E_{ss}. \tag{44} \]

In the NDOL approximation, the pure state energies are simple linear combinations of the eigenenergies. Making all of the necessary substitutions and rearrangements in Eq. (42), we achieve the ensemble representation:

\[ E_{\text{NDOL}}^{\text{NDOL}}(q) = E_{gs} + \omega(q, q_{gs}) (E_{ss} - E_{gs}), \tag{45} \]

where the occupation number is

\[ \omega(q, q_{gs}) = q_{gs} - 2 \sqrt{q(1 - q)q_{gs}(1 - q_{gs}) + q (1 - 2q_{gs})}. \tag{46} \]

To see that Eq. (45) has the desired properties, note that \( \omega(q, q_{gs}) \) lies between 0 and 1 over the interval [0,1] in \( q \), it is 0 at \( q = q_{gs} \), and \( \partial \omega(q, q_{gs}) / \partial q \) at \( q = q_{gs} \) is also 0. These properties are illustrated in Fig. 2. Taking into account our restriction to a 2-state model, if we apply atom decomposition to the eigenenergies, we would obtain the same form as Eq. (4), with \( \omega_{A^0} = 1 - \omega(q, q_{gs}), \omega_{A^+} = \omega(q, q_{gs}), \) and \( \omega_{A^-} = 0 \). Importantly, the representation is in terms of eigenenergies instead of energy matrix elements. Furthermore, as \( q_{gs} \) approaches 0, as in the assumed dissociation limit for AB, \( E_{\text{NDOL}}^{\text{NDOL}}(q) \) becomes linear in \( q \). Another representation of the occupation number, Eq. (46), is significant. By using the relationship \( q = \gamma^2 / (1 + \gamma^2) \) from Eqs. (38), we obtain

\[ \omega (\gamma, q_{gs}) = \frac{(\gamma - q_{gs})^2}{(1 + \gamma^2)(1 + \gamma_{gs}^2)}. \tag{47} \]

As is necessary physically, the occupation number is 0 when \( \gamma = q_{gs} \), where \( q_{gs} \) corresponds to \( q_{gs} \). The complete generalization of Eq. (47) is equivalent to following the process steps outlined above.

Eqs. (43) and (44) can be inverted. Inversion gives

\[ E_{\text{NDOL}}^{\text{NDOL}}(q) = \omega_{cc} H_{cc} + \omega_{ii} H_{ii} \tag{48} \]

where

\[ \omega_{cc} = (1 - \omega - q_{gs}) / (1 - 2q_{gs}) \tag{49} \]
FIG. 2: 2-state EVB-NDOL occupation number, Eq. (46), in the ensemble representation of $E_{\text{NDOL}}^{(q)}$, Eq. (45). Charges are dimensionless.

and

$$\omega_{ii} = (\omega - q_{gs})/(1 - 2q_{gs}) . \quad (50)$$

Consistent with the conclusions of MM and physical necessity, the coefficients are not positive-semidefinite. Fig. 3 illustrates Eq. (49), the coefficient for the covalent state. In order to cover the range of energies between $E_{gs}$ and $E_{xs}$, the coefficients of $H_{cc}$ and $H_{ii}$ cannot possibly be positive-semidefinite. The coefficients are not defined for $q_{gs} = 1/2$. At that value of the ground-state charge, $H_{cc}$ must equal $H_{ii}$.

It is interesting to see how the present results connect with classical electrostatic potentials (Eq. (3)). We can expand Eq. (46) locally as a function of $q$ as long as the expansion point is not zero or one. First,

$$\frac{\partial \omega(q, q_{gs})}{\partial q} = -(1 - 2q) \sqrt{\frac{q_{gs}}{(q (1 - q))}} + 1 - 2q_{gs} . \quad (51)$$

The obvious value about which to expand is $q_{gs}$. By construction, $\partial \omega(q, q_{gs})/\partial q|_{q_{gs}} = 0$. Second,

$$\frac{\partial^2 \omega(q, q_{gs})}{\partial q^2} = \sqrt{\frac{q_{gs}}{2 (q (1 - q))}} . \quad (52)$$

If we evaluate Eq. (52) at $q = q_{gs}$, as $q_{gs} \rightarrow 0$ or 1, the expansion behaves badly. Alternatively, we might try expanding about $q = 1/2$, for the physically appealing reason that $dE_{\text{NDOL}}^{(q)}/dq|_{q=1/2} = IP_A^* - EA_B^*$. Then

$$\frac{\partial^2 \omega(q, q_{gs})}{\partial q^2} \bigg|_{q=1/2} = \sqrt{2q_{gs}} \left(1 - q_{gs}\right) . \quad (53)$$

To second order,

$$E_{\text{NDOL}}^{(q)} \approx E_{gs}$$

$$+ \left(q_{gs} - (1 - \sqrt{2}/8) \sqrt{q_{gs} (1 - q_{gs})}\right)$$

$$+ \sqrt{2q_{gs} (1 - q_{gs}) q^2/2} (E_{xs} - E_{gs}) . \quad (54)$$

This quadratic expansion has the form of Eq. (3) and behaves well physically under dissociation, even to the extent of preserving the dissociation limit. The electronegativity, hardness, and electrostatic contributions are embedded in the eigenenergies. The equivalent expansion of Eq. (48) might be more revealing in displaying these contributions. A key observation is that the quadratic term vanishes completely at infinite separation ($q_{gs} \rightarrow 0$) and only the linear dependence survives. Again, the survival of the linear charge dependence is consistent with PPLB. There is no residual atomic hardness contribution as has appeared in many implementations of Eq. (3).4–6,23,34 We speculate that a hardness contribution might be missing because we have considered only a 2-state model instead.
of a 3-state model. Our reasoning behind this speculation is discussed below. We have ruled out the possibility that introducing the NDOL approximation prior to making the expansion is a factor. Nevertheless, adding a third state must not change the fact that the coefficient of the quadratic term must go zero in order for the results to be consistent with PPLB. Likewise, any hardness contributions to the linear term must be scaled by a coefficient that goes to zero at large $R$. Clearly, one cannot approximate either Eq. (26) or (39) quadratically to arbitrary accuracy in a global sense.

### B. General Definition of the Energy for a Given Charge

Next we consider the densities and their energies in the NDOL approximation. From Eq. (20) we have

$$\rho_{\text{NDOL}}^\gamma(q) = \rho_{cc} + \sqrt{\gamma^2 \rho_{ii}} / (1 + \sqrt{\gamma^2}) .$$

(55)

Thus, from Eq. (38),

$$\rho_{\text{NDOL}}^\gamma(q) = \rho_{cc} + q (\rho_{ii} - \rho_{cc}) .$$

(56)

By symmetry in Eq. (55), $\rho(\gamma) = \rho(-\gamma)$, but, from Eq. (8), $E(\gamma) \neq E(-\gamma)$. To address this difficulty, MM appeal to a maximum entropy principle. We prefer instead to appeal to CS-DFT. Accordingly, CS-DFT instructs us to place the $\Gamma_{\text{NDOL}}^\gamma(q)$ into groups defined by the density that they produce. Since $\Gamma_{\text{NDOL}}^\gamma(q)$ and $\Gamma_{\text{NDOL}}(-\gamma)$ both yield the same density, $\rho_{\text{NDOL}}^\gamma(q)$, they are grouped together. The energy assigned to $E_{\text{NDOL}}[\rho_{\text{NDOL}}^\gamma(q)]$ is the minimum of the energies for these two $\Gamma$’s:

$$E_{\text{NDOL}}[\rho_{\text{NDOL}}^\gamma(q)] = \min \{ \langle H, \Gamma_{\text{NDOL}}^\gamma(q) \rangle, \langle H, \Gamma_{\text{NDOL}}(-\gamma(q)) \rangle \} .$$

(57)

The ground state energy is then the minimum over all $q$ of $E_{\text{NDOL}}[\rho_{\text{NDOL}}^\gamma(q)]$. When differential overlap ($\rho_{ii} \neq 0$) is included, the densities appear to become unique for $\gamma$’s of different signs.

Note that a similar procedure could be followed for MM’s 3-state case at the ZDO level that they assume. See also Ref. 33. Even with this comparatively simple extension, the situation is less clear than in the 2-state case. Many densities may have the same charge on the atoms. By again appealing to CS-DFT, one can assign $E(q)$ for a given $q$ by minimizing over the energies of all densities with the same $q$. That is, as a straightforward extension of CS-DFT, we very generally define

$$E(q) = \min_{\rho(q, \delta) \rightarrow q} E_{\text{CS-DFT}}[\rho(q, \delta)] \ ,$$

(58)

where $\delta$ represents all of the other undetermined parameters of the density $\rho(q, \delta)$. By minimizing over $\delta$, one may introduce dependencies on the energy matrix elements that are absent from the present 2-state model. This is the reason behind our speculation that the isolated-atom hardnesses do not appear in Eq. (54) because of the limitations of the 2-state model. One advantage of the charge-generalized CS-DFT approach over a maximum entropy principle is that the true ground state properties can be preserved in the same way that the ground state energy can be recovered — by minimizing over all allowed densities in conventional CS-DFT.

### C. Examples: HF, LiH, and H₂

First we discuss modeling the polar molecules HF and LiH in the NDOL approximation. Then, for the non-polar molecule H₂, we compare the NDOL and general cases. There we utilize the Weinbaum wavefunction. It provides an excellent illustration of the ambiguities encountered in defining the resonance state wavefunctions. We also examine various approximations for $\delta N_{c_i A}$ and examine the change in the charge dependence as a function of $R$.

For HF and LiH, we use RKR curves to define $E_{gs}$ and $E_{ex}$. For the $\text{X}^+$ states of HF, the RKR data are from Di Lourando and Douglas; and for the $\text{X}^+$ and $\text{A}^+$ states of LiH, the RKR data are from Chan et al. and Pardo et al. We use the calculations of Ref. 19 to define $q_{gs}$. These data are shown in Figs. 4 and 5. The $\text{B}^+$ and $\text{A}^+$ states dissociate to ions, $\text{H}^+$ and $\text{F}^+$ and Li$^+$ and H$^-$, respectively. To allow matching of the different spatial ranges of the data, analytical fits for the energy curves were made with the Rose and Rose-ionic functional forms. The charge data were fit with the functional form, $K_0 + (K_1 - K_0)(qK^2/(1 + (qK^2 + K_3K_2)))$, where the $K$’s are fitting parameters. $H_{ex}$ and $H_{ii}$ were computed from Eqs. (43) and (44), respectively. In both cases, $H_{cc}$ and $H_{ii}$ cross at $q_{gs} = 1/2$ and meet their respective states at the dissociation limits. Representative shapes of the charge dependence for given values of $R$ are shown in Figs. 6 and 7. The correct dissociation-limit behavior is observed in both cases. In simulations where each atom remains within a unit charge interval, the NDOL model might therefore prove to be useful, although it is unlikely to be quantitative. The difference in charge transfer characteristics between the present results and PPLB can be seen by contrasting the $R = 3$ Å curve of Fig. 7 with the $R = 3.1$ Å curve of their Fig. 1. The transfer is more gradual here and passes through fractional charge states, compared to PPLB which is very sharp and passes directly from a completely covalent state to a completely ionic one.

Next we consider H₂. The simplest valence bond form for the covalent state $\psi_c^{(1)} = (\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2))/(2 + 2S_{AB})^{1/2}$, where $S_{AB}$ is the atomic orbital overlap. Our naive inclination for the ionic state is to use the familiar $\psi_i^{(1)} = (\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2))/(2 + 2S_{AB})^{1/2}$. The total wavefunction is $\psi = c(\psi_c + \gamma\psi_i)$. It turns out that the total densities for
both states are identical: $\rho_{cc} = \rho_{ii} = (\phi_A^2 + 2 S_{AB} \phi_A \phi_B + \phi_B^2)/(1 + S_{AB}^2)$. (Designation of the electronic coordinate is suppressed in the densities for readability.) The interference density is $\rho_{ci} = ((\phi_A^2 + \phi_B^2) S_{AB}^2 + 2 \phi_A \phi_B)/ (1 + S_{AB}^2)$.

If we assume a simple Hirshfeld partitioning as our total density decomposition strategy,\textsuperscript{18,61,63} then it is natural to assume that each component of the density is likewise scaled by $\phi_A^2/(\phi_A^2 + \phi_B^2)$ in order to obtain the atom A contribution. However, we find that because of symmetry, $\delta N^*_{ci,A} = 0$, which cannot be correct. Of course, the problem is that the assumption about the Hirshfeld partitioning form is incorrect. This partitioning cannot lead to a value of $\rho_{ii,A}$ that integrates to $N_{AB} = 1 = 0$. A different partitioning must be chosen to force all of the density in $\rho_{ii}$ to belong to atom B. In addition, we know the optimum values of $\gamma$ for these two resonance states\textsuperscript{56,57} and that these values correspond to $q = 0$. For instance,
at the equilibrium H$_2$ separation, $\gamma_{\text{opt}} = -0.26$, with the resonance energy defined as positive.$^{56}$ From Eq. (23), we also can deduce that $\delta N_{\mathrm{ci},A}^* = \gamma_{\text{opt}}/2 = -0.13$. This analysis hints at the subtle properties that the density decomposition must possess if one implements explicit decomposition of $\rho_{\mathrm{ci}}$.

Another immediate insight is that any fixed value of $\gamma$ applied within $\psi$ leads to an acceptable covalent state. Clearly, the energy change caused by a polarization of the H$_2$ charge density will differ depending on one’s choice for the resonance state. Similarly, the density decomposition will show some sensitivity to this choice.

Of course, a more sensible choice for the ionic state is $\psi^{(2)}_i = \phi_\mathrm{B}(1)\phi_\mathrm{B}(2)$ because, for a homonuclear diatomic, the charged states correspond to broken charge-symmetry states. Even in this simple case, the partitioning of $\rho_{\mathrm{ci}}$ may be nontrivial.

As a final consideration, we illustrate the influence of overlap on ionicity. For this purpose, we utilize our original choices for covalent and ionic wavefunctions, $\psi^{(1)}_c$ and $\psi^{(1)}_i$. The overlap integral is estimated in terms of $S_{\mathrm{AB}}$ as given above. Taking $\phi(r) = \sqrt{\alpha/\pi} \exp(-\alpha r)$, the atomic overlap is $S_{\mathrm{AB}}(a) = \exp(-a)(1 + a + 1/3 a^2)$, where $a = \alpha R$. The effect of overlap is shown in Fig. 8 as $\gamma(q)/(1 - q)$. There it can be seen that the NDOL approximation becomes accurate beyond approximately 2 Å. The relatively large range of $R$ for which the NDOL approximation is accurate is due in no small part to the fact that $S_{\mathrm{ci}}$ depends on the square of $S_{\mathrm{AB}}$. This broad range of accuracy and the fact that Eqs. (45) and (46) are well-behaved for any $R$ makes it tempting to use NDOL in general. However, near equilibrium bond lengths, Fig. 8 indicates that overlap effects should not be ignored.

VI. CONCLUSION

In order to apply chemical potential equalization in a simulation that involves conditions far from reference states, the potential energy must be defined for arbitrary values of the charges. To address this challenge, we have derived a new charge-dependent pair potential from a 2-state empirical valence bond model. The charge is defined from a decomposition of the density into constituent contributions. The explicit charge dependence is deduced by requiring consistency between the density decomposition and the wavefunction descriptions of the ground state. The energy expression can be made valid for any range of charge of interest. The decomposition theme is further extended to define the energy of individual constituents, again by requiring consistency between the density decomposition and the wavefunction descriptions. The energy of the system for a given value of charge is made unique by appealing to constrained search density functional theory. An examination of the model shows linear dependence on charge at the dissociation limit, as well as discontinuous behavior in the derivative of the energy as a function of charge at integer values of the charge. This behavior is consistent with the analysis of Perdew et al.$^{2,33}$ The potential energy for arbitrary charge and separation of the constituents can be represented as an ensemble average of the eigenenergies with a nonlinear, analytical dependence of the occupation number on charge. The representation of the potential energy in terms of the pure-state energy matrix elements is possible, but, by physical necessity, cannot be expressed as an ensemble average with positive semidefinite coefficients.

To determine a pair potential for all values of $q$ and $R$ with this method, one needs five reference or calibration curves. These most often will be computed values of the ground-state energy, the charges along the ground-state energy curve, the resonance state overlap integral, the covalent energy and ionic energy. Measurements of ground and ionic-excited state energies and charges can also be used. The covalent energy and ionic energy are determined for integer charges only. To determine a point on the potential energy curve, a well-defined five step procedure is followed using the five input curves. An immediate application of the method could be to construct the reference potential curves for the A$_2$, B$_2$, and AB systems. Simulations on arbitrary mixtures of these three types of systems under nonequilibrium initial conditions would then be possible. Chemical potential equalization would be used to dynamically adjust the charges of the constituents. More generally, we envision the present approach as forming the basis for a new class of charge-dependent empirical potentials for use in large-scale simulations of reactive systems.
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For an arbitrary set of basis wavefunctions, there is no simple way to determine which wavefunctions map to which densities. Even in a finite basis set, pathological cases are possible.


