Partition theory: A very simple illustration

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We illustrate the main features of a recently proposed method based on ensemble density functional theory to divide rigorously a complex molecular system into its parts [M.H. Cohen and A. Wasserman, J. Phys. Chem. A 111, 2229 (2007)]. The illustrative system is an analog of the hydrogen molecule in which analytic expressions for the densities of the parts (hydrogen “atoms”) are found along with the “reactivity potential” that enter the theory. While previous formulations of Chemical Reactivity Theory lead to zero, or undefined, values for the chemical hardness of the isolated parts, we demonstrate they can acquire a finite and positive hardness within the present formulation.

1. INTRODUCTION

In a series of recent papers [1, 2, 3], two of us have developed a rigorous method for dividing a complex system into its parts based on density-functional theory [4, 5, 6, 7, 8]. The underlying theory, partition-theory (PT), was used to construct a formulation of chemical reactivity theory (CRT) [3] which, for the first time, is consistent with the underlying density-functional theory [9, 10, 11, 12, 13].

In PT [1, 2, 3], a sharp definition of the individual parts into which the whole system is partitioned is achieved first by selecting the nuclei of each putative part and maintaining these in the positions in which they occur in the whole and then requiring that the sum of the electron densities of the parts, each of which is treated as though isolated, add up exactly to the electron density of the whole (the density constraint). The electron densities of the parts are then to be determined by minimizing the sum of the density functionals of the individual parts with respect to the densities of the parts subject to the density constraint. The density functional used, that of ref. [8] (PPLB), allows for the existence of noninteger numbers of electrons on each part, necessary e.g. for the definitions of electronegativity [12] and hardness [13], key indices of chemical reactivity [3], and for incorporating covalent bonding between inequivalent parts.

The minimization proceeds via a Legendre transformation, which introduces a reactivity potential $v_R(r)$ as the Lagrange multiplier of the density constraint. Thus, the formalism can become computationally complex. First the electron density of the whole system must be determined. Then, the densities of the parts must be determined simultaneously with $v_R$, all of which is required to set the stage for the determination of mutual reactivities between parts, though certain self-reactivities can be determined for each species alone without reference to a larger system [3].

Accordingly, in the present paper, we develop the partition theory in detail for an extremely simple system to exhibit its main features explicitly. The illustrative system is an analog of the hydrogen molecule in which the electrons move in one dimension along the molecular axis without interacting, and the nuclear Coulomb potentials are replaced by attractive delta-function potentials. As a consequence of these extreme simplifications, many quantities of interest can be determined analytically in a transparent manner, including the electron density of the molecule, of its parts (the “atoms”), and the reactivity potential at all internuclear separations.

In Section 2, the model is defined and the molecular density obtained. In Section 3, the parts are defined, shown to have one electron each, and a polar representation for their wave functions found which facilitates the minimization. In Section 4, the minimization is carried out, resulting in an Euler equation for the polar angle $\beta(x)$ of that representation. $\beta(x)$ is found in Section 5 and used to determine the reactivity potential $v_R$ in Section 6. The principle of electronegativity equalization formulated in refs. [2] and [3] is shown to hold in Section 7. Also in Section 7, the hardness [3] of the isolated H atom is calculated, shown to be nonzero, and correlated with the strength with which its electron is bound. Thus, despite the fact that the model is a caricature of the real system, meaningful features of the partition theory are indeed illustrated by it, as discussed in the concluding Section, 8.
2. 1D-H₂: INDEPENDENT ELECTRONS MOVING IN ATTRACTIVE δ-FUNCTION POTENTIALS IN ONE DIMENSION

Our task is to partition an analog of the H₂ molecule in which two electrons move independently in δ-function nuclear potentials in one dimension into parts, analogs of H atoms. Each H atom has, by symmetry, only one electron, so the need for the PPLB density functional is avoided. Indeed no explicit use of density-functional theory is required for the molecule or the atoms. The ground-state wave function ψ₀ and energy E₀ of an isolated H atom are (atomic units are used throughout):

$$ψ₀(x) = \sqrt{Ze}^{-Z|x|} \quad \text{and} \quad E₀ = -Z^2/2 . \quad (2.1)$$

In Eq. (2.1), (−Z) is the strength of the δ-function potential. To draw the analogy closer to real hydrogenic atoms, one could equate Z to the nuclear charge.

The ground-state energy $E(N = 1)$ of one electron moving independently in the two δ-function potentials centered at $x = ±a$ is $E(N = 1) = -κ²/2$, where κ satisfies

$$κ = 2Z/(1 + \tanh κa) . \quad (2.3)$$

The corresponding wavefunction is:

$$ψ_M(x) = Be^{κ(a−|x|)} , \quad |x| > a$$

$$ψ_M(x) = B\cos\frac{κa}{\cosh κa} , \quad |x| < a \bigg\} , \quad (2.4)$$

where

$$B = κ^{1/2} \left[ 1 + \frac{κa}{\cosh^2 κa} + \tanh κa \right]^{-1/2} . \quad (2.5)$$

Note that $κ → 2Z$ as $a → 0$ (united atom limit) and $κ → Z$ as $a → ∞$ (separated atom limit).

The two-electron molecular electron density is given by:

$$n_M(x) = 2|ψ_M(x)|^2 , \quad (2.6)$$

and the total energy of the molecule is

$$E_M(N = 2) = 2E_M(N = 1) = -κ² . \quad (2.7)$$

where $N$ is the number of electrons in the molecule. The chemical potential of the molecule is therefore

$$μ_M = E(2) − E(1) = E(1) = -κ²/2 . \quad (2.8)$$

3. PARITY DECOMPOSITION

We now partition the molecule into two parts $α = 1, 2$, each having a real one-electron wave function $ψ_α$, localized around $−a$ and $+a$ respectively, so that $n_M(x)$ is given by

$$n_M(x) = n_1(x) + n_2(x) , \quad (3.1)$$

where $n_α(x)$ is the electron density of each part $α = 1, 2$ treated independently. The “atomic” wavefunctions are given by:

$$ψ_α(x) = \sqrt{n_α(x)} . \quad (3.2)$$

They are mirror images of each other,

$$ψ_2(x) = ψ_1(−x) , \quad (3.3)$$

and both are normalized.

We now decompose the $ψ_α$ into their symmetric, $ψ_s(−x) = ψ_s(x)$, and antisymmetric, $ψ_α(−x) = −ψ_α(x)$, parts by a rotation within the function space they span,

$$ψ_1 = \frac{1}{\sqrt{2}}(ψ_s + ψ_a) , \quad ψ_2 = \frac{1}{\sqrt{2}}(ψ_s − ψ_a) ; \quad (3.4)$$

$$ψ_s = \frac{1}{\sqrt{2}}(ψ_1 + ψ_2) , \quad ψ_a = \frac{1}{\sqrt{2}}(ψ_1 − ψ_2) . \quad (3.5)$$

The rotation leaves “lengths” within the space invariant so that

$$n_M = ψ_s^2 + ψ_a^2 . \quad (3.6)$$

We next introduce $β = β(x)$, a polar angle in the function space,

$$ψ_s = \sqrt{n_M} \cos β , \quad ψ_a = \sqrt{n_M} \sin β , \quad (3.7)$$

so that

$$ψ_{1,2} = \sqrt{n_M/2} (\cos β ± \sin β) . \quad (3.8)$$

Because the $ψ_α$ are non-negative, $|β|$ cannot exceed $π/4$. Furthermore $β$ must be an odd function of $x$, to ensure $ψ_α$ is also odd. This also guarantees normalization of $ψ_α$.

4. THE EULER EQUATION FOR $β(x)$

To apply PT [2, 3], begin with the original Hamiltonian

$$H = \frac{1}{2} \sum_{i=1,2} p_i^2 − Z \sum_{i=1,2} [δ(x_i − a) + δ(x_i + a)] . \quad (4.1)$$

Then divide the system into overlapping regions, each with a given number of electrons. In this case, we choose one electron on the left, and the other on the right. Thus we have two 1-electron problems:

$$H_α = \frac{p_α^2}{2} + v_α , \quad v_{1,2} = −Zδ(x ± a) . \quad (4.2)$$

The PT problem is to minimize

$$E = ⟨ψ_1, H_1 ψ_1⟩ + ⟨ψ_2, H_2 ψ_2⟩ , \quad (4.3)$$

subject to normalization of the wavefunctions, but also to the constraint that the total density equal the original molecular density, Eq. (3.6). (Without the latter constraint, we’d obviously find $ψ_{1,2} = ψ_0(x = ±a)$.)
polar representation of Sec.3, both density and normalization constraints are automatically satisfied, so the partition problem becomes simply minimizing $\mathcal{E}$ as a functional of $\beta$. That functional is

$$\mathcal{E} = \int dx \left\{ \frac{1}{2} \left[ \frac{n_M}{4} - \frac{1}{2} n_M^2 + n_M \beta' - n_M \beta'' \right]^2 \right\} + \frac{1}{2} n_M \left[ (v_1 + v_2) + (v_1 - v_2) \sin 2\beta \right].$$  \hspace{1cm} (4.4)

Varying it yields

$$\delta \mathcal{E} = \int dx \{ n_M \beta' \delta \beta' + (v_1 - v_2) n_M \cos 2\beta \delta \beta \}. \hspace{1cm} (4.5)$$

Integrating by parts, as usual, leads to

$$\delta \mathcal{E} = 2n \beta' \delta \beta'_{x=+\infty} + \int dx \left\{ \frac{d}{dx} \left( n_M \frac{d \beta}{dx} \right) + (v_1 - v_2) n_M \cos 2\beta \delta \beta \right\}. \hspace{1cm} (4.6)$$

For $\mathcal{E}$ to be stationary with respect to arbitrary variations $\delta \beta$ of $\beta$, both terms contributing to $\delta \mathcal{E}$ in Eq. (4.6) must vanish. The Euler equation which results from the vanishing of the second term in Eq. (4.6) is

$$- \frac{d}{dx} \left( n_M \frac{d \beta}{dx} \right) + (v_1 - v_2) n_M \cos 2\beta = 0, \hspace{1cm} (4.7)$$

$$\frac{d}{dx} \left( n_M \frac{d \beta}{dx} \right) + Z (\delta(x-a) - \delta(x+a)) \times$$

$$\times n_M \cos 2\beta = 0. \hspace{1cm} (4.8)$$

The vanishing of the first term in Eq. (4.6) sets the boundary condition at infinity on the Euler equation (4.8). There are two possibilities, the vanishing of $\beta'$ at infinity or the fixing of $\beta$ there so that $\delta \beta$ must vanish. As we shall see in Section 5, imposing the latter results in an unacceptable divergence in $\beta'$ at infinity. We therefore impose the boundary condition

$$\beta'(x) = 0, \hspace{0.5cm} |x| = \infty. \hspace{1cm} (4.9)$$

5. SOLVING FOR $\beta(x)$

Eq. (4.8) becomes

$$\frac{d}{dx} \left( n_M \frac{d \beta}{dx} \right) = 0, \hspace{0.5cm} |x| \neq a, \hspace{1cm} (5.1)$$

subject to the boundary conditions Eq. (4.9) and

$$\beta(a^{-}) = \beta(a^{+}) \equiv \beta_a$$

$$\beta'(a^{-}) - \beta'(a^{+}) = Z \cos 2\beta_a \hspace{1cm} x = a, \hspace{1cm} (5.2)$$

$$\beta(-a^{-}) = \beta(-a^{+}) = -\beta_a$$

$$\beta'(-a^{-}) - \beta'(-a^{+}) = Z \cos 2\beta_a \hspace{1cm} x = -a. \hspace{1cm} (5.3)$$

The general solution of (5.1) is

$$\frac{d\beta(x)}{dx} = \frac{c_1}{n_M(x)}, \hspace{1cm} (5.4)$$

$$\beta(x) = \int^x dx' \frac{c_1}{n_M(x')} + c_2. \hspace{1cm} (5.5)$$

where $c_1$ and $c_2$ are constants. As implied above in Section 4, if $c_1$ does not vanish $\beta'$ diverges exponentially at infinity, according to Eq. (5.4), because $n_M$ goes exponentially to zero, so, in accordance with Eq. (4.9), $c_1$ vanishes for $|x| > a$, and $\beta(x)$ is constant there,

$$\beta(x) = \beta_a, \hspace{0.5cm} x > a$$

$$\beta(x) = -\beta_a, \hspace{0.5cm} x < -a. \hspace{1cm} (5.6)$$

For $|x| < a$ we can rewrite Eq. (5.6) as

$$\beta(x) = \int^x dx' \frac{c_1}{n_M(x')} - \beta_a, \hspace{1cm} (5.7)$$

which implies that

$$\beta_a = \frac{1}{2} \int^a dx \frac{c_1}{n_M(x)}. \hspace{1cm} (5.8)$$

From (5.8) we can relate $c_1$ to $\beta_a$ via Eq. (2.6),

$$c_1 = \frac{2\kappa B^2 \beta_a}{\cosh^2 \kappa a \tanh \kappa a}. \hspace{1cm} (5.9)$$

Inserting (5.9) for $c_1$ into Eq. (5.4) and the result into the BC (5.2) or (5.3) produces an equation for $\beta_a$,

$$\beta_a = \frac{Z}{2\kappa} \sinh 2\kappa a \cos 2\beta_a. \hspace{1cm} (5.10)$$

Inserting Eqs. (5.9) and (2.6) into Eq. (5.7) yields the remarkably simple result

$$\beta(x) = \frac{\tanh \kappa x}{\tanh \kappa a} \beta_a, \hspace{0.5cm} 0 < |x| < a. \hspace{1cm} (5.11)$$

Eqs. (5.6), (5.10), and (5.11), together with Eq. (2.6), provide a complete analytic solution for $\beta(x)$ and through Eqs. (5.5) and (5.8) for the $\psi_a$. In Fig. 1 we show $n_M$, $n_1$ and $n_2$ vs. $x$ for $Z = 1$ and $a = 1$. We see that each localized density spreads into the neighboring region, and looks quite similar to an atomic density. To see the differences from isolated atomic orbitals, in Fig 2 we make the distance smaller ($a = 0.3$), and show the right-side “atomic” orbital $\psi_1(x)$ (solid line) and compare it with the pure exponential orbital $\psi_0(x)$ of Eq. (2.4) (dashed line). The orbital $\psi_1$ resembles $\psi_0$ and tends to it for large $a$, but is distorted with respect to it for small $a$. Its maximum is still a cusp at $x = a$, but it also shows a second cusp at $x = -a$. Since $\kappa > Z$ always (Eq. (2.6)), and either $\psi_1$ or $\psi_2$ is proportional to $\psi_M$ for $|x| > a$, where $\beta = \beta_a$ is constant, the PT atomic densities and orbitals decay more rapidly than isolated atoms. Since
Qualitatively, from Eq. (5.11), Fig. 3, we show enhanced density between the ‘nuclei’, due to bonding. In their normalization is the same, this in turn means en-
dominates on its own side, consuming the entire density region. But if \( \beta \) is small, both ‘atoms’ share the density in each outside region. If \( \beta_a \) is small, both ‘atoms’ share the density in each outside region. But if \( \beta_a \) is close to \( \pi/4 \), each atom dominates on its own side, consuming the entire density there.

\[
\beta(x) \simeq \beta_a \frac{x}{a} , \quad x < \min(1/\kappa, a) = \beta_a , \quad x > \min(1/\kappa, a)
\]

and if \( Za >> 1 \) (large separation), \( \beta_a \simeq \pi/4 \) while if \( Za << 1 \) (small separation), \( \beta_a \simeq \alpha \). The interpretation of these results is given in terms of Eq. (5.11), outside the bond region. If \( \beta_a \) is small, both ‘atoms’ share the density in each outside region. But if \( \beta_a \) is close to \( \pi/4 \), each atom dominates on its own side, consuming the entire density there.

6. THE REACTIVITY POTENTIAL

The one-electron wave functions \( \psi_1(x) \) and \( \psi_2(x) \) are not eigenstates of the part-Hamiltonians \( H_1 \) and \( H_2 \) of Eq. (4.2). The natural question arises: What are they eigenstates of? The partition theory of refs. [1, 2, 3] dictates that they are eigenstates of the modified single-electron Hamiltonian \( H^R = p^2/2 + V_{\alpha} \), \( \alpha = 1, 2 \):

\[
\left( \frac{p^2}{2} + V_{\alpha} \right) \psi_\alpha = \mu_M \psi_\alpha , \quad \alpha = 1, 2 .
\]

\[
V_{\alpha} = v_c + v_R
\]

where the eigenvalue, regardless of the part \( \alpha \), is precisely equal to the molecular chemical potential \( \mu_M \) of Eq. (2.8). The potential \( v_R(x) \) is the reactivity potential that we now construct explicitly. Summing over \( \alpha \) and dividing by \( \psi_1 + \psi_2 \) yields a symmetric expression for \( v_R \),

\[
v_R = \mu_M - \frac{1}{\psi_1 + \psi_2} \left( \frac{p^2}{2} (\psi_1 + \psi_2) - \frac{v_1 \psi_1 + v_2 \psi_2}{\psi_1 + \psi_2} \right) .
\]

\( \psi_1 \) and \( \psi_2 \) can be reexpressed in terms of \( \psi_s \) and \( \psi_a \), Eq. (5.5). Noting that

\[
n_M = 2 \psi^2 \]

using Eq. (3.7) for \( \psi_s,a \), and taking the \( \delta \)-function character of \( v_\alpha \) into account results in

\[
v_R = \mu_M + \frac{1}{2 \psi_M \cos \beta} \frac{d^2}{dx^2} (\psi_M \cos \beta) + \frac{1}{2} (v_1 + v_2)(1 + \tan \beta_a) .
\]

The molecular wave function \( \psi_M \) satisfies the Schrödinger equation,

\[
- \frac{1}{2} \frac{d^2}{dx^2} (v_1 + v_2) \psi_M = \mu_M \psi_M ,
\]

which can be used to transform Eq. (6.5) to

\[
v_R = - \frac{1}{2} \left\{ \left[ \frac{2}{\psi_M} \frac{d\psi_M}{dx} \frac{db}{dx} + \frac{d^2\beta}{dx^2} \right] \tan \beta + \left( \frac{d\beta}{dx} \right)^2 \right\} + \frac{1}{2} (v_1 + v_2)(1 - \tan \beta_a) .
\]

Using Eq. (6.4), the Schrödinger-like equation for \( \beta \), Eq. (5.8), can be rewritten as

\[
- \frac{1}{2} \left\{ \frac{2}{\psi_M} \frac{d\psi_M}{dx} \frac{db}{dx} + \frac{d^2\beta}{dx^2} \right\} + \frac{1}{2} (v_1 - v_2) \cos 2\beta_a = 0 .
\]

Multiplying Eq. (6.8) by \( \tan \beta \), invoking the oddness of \( \beta \) and the \( \delta \)-functions in \( v_1 \) and \( v_2 \), and subtracting the result from Eq. (6.7) yields for \( v_R \)

\[
v_R = - \frac{1}{2} \left( \frac{d\beta}{dx} \right)^2 + \frac{1}{2} (v_1 + v_2) \left[ 1 - (1 + \cos 2\beta_a) \tan \beta_a \right] .
\]
Inserting our previous result for \(\beta(x)\), Eqs. (6.6) and (5.11) into (6.9) yields an explicit result for \(v_R\),

\[
v_R = \frac{\mu_M \beta^2 a^2}{\tanh^2 \kappa a} \frac{\theta(a - |x|)}{\cosh^4 \kappa x} + \frac{1}{2} (v_1 + v_2) [1 - \sin 2/\beta a],
\]

where \(\theta(y) = 0\) for \(y < 0\), 1 for \(y > 0\) is the Heaviside step function. Eq. (6.10) shows that \(v_R(x)\) vanishes for \(|x| > a\), has attractive \(\delta\)-functions at \(\pm a\) whose weights increase monotonically from 0 to \(\frac{1}{2} Z\) as \(Z a\) decreases from infinity to zero, and has an attractive inverse \(\cosh^4(x)\) component for \(|x| < a\). For the united atom case, \(Z a \downarrow 0\), \(v_1 + v_R = v_2 + v_R = 2v_1\) simply reproduces the molecular potential, and \(\psi_1 = \psi_2 = \psi_M\) as they should. Figure 4 displays \(v_R\) vs. \(x\) for fixed \(Z = 1\) and representative values of \(a\). The reactivity potential is almost flat for small separations, a wide well in between the two atoms for intermediate separations, and a narrow well that is far from both atoms at large separations. Figure 5 displays the weights of the \(\delta\)-function components of \(v_R\) divided by \(Z\) vs. \(a\).

As shown in ref. [3], the Kohn-Sham (KS) HOMO eigenvalue of each part must be identical to the chemical potential of the whole in the added presence of \(v_R\). In our simple example, the KS potential of a part reduces to the nuclear \(\delta\)-function potential of one H atom. Adding \(v_R\) to the nuclear potential must therefore transform the HOMO energy \(E_0\), Eq. (2.2), of the isolated atom to the more negative HOMO energy of the molecule \(E(N = 1) = -v^2/2\), which is its chemical potential (Eq. (5.2)). \(v_R\) must be attractive to do that, which it is, from Eqs. (6.9) and (6.10). In our simple example, \(v_R\) makes the delta function of the atom more negative, adds the attractive inverse \(\cosh^4\) potential between the atoms, and adds an attractive ghost delta function at the position of the other atom to force the wave function to decay sufficiently rapidly outside the molecule.

In the limit of infinite separation \(v_1 + v_R\) reduces to \(v_1\) and \(v_2 + v_R\) reduces to \(v_2\), except for \(|x| < a\), where the attractive potential

\[
v_R(x) = \frac{\pi^2 E_0}{16} \frac{1}{\cosh^4 Zx}, \quad |x| < a,
\]

persists. This potential has at least one additional bound state, but with binding energy less than \(|E_0|\). Thus it is unoccupied, and does not affect our results. The \(a\)-dependence of this state’s energy is shown for fixed \(Z\) in Fig. 6. For very large separation between the atoms, it is localized at the center of the inverse \(\cosh^4(x)\) component of \(v_R\), but it rapidly delocalizes for smaller separations. In particular, for \(Z = 1\), it is highly delocalized when \(a <\sim 1.4\), where it vanishes into the continuum.

7. SUSCEPTIBILITY AND HARDNESS

Having found the reactivity potential, we now illustrate the construction of reactivity indices. In the CRT of ref. [3], each part \(\alpha\) is represented by an ensemble of
PPLB type containing contributions with only two integer electron numbers, \( p_\alpha \) and \( p_{\alpha+1} \). The principle of electronegativity equalization is expressed as the equality of the chemical potential of each part in the presence of the reactivity potential, \( \mu^R_\alpha \), to the chemical potential of the molecule, \( \mu_M \),

\[
\mu^R_\alpha = \mu_M , \quad \forall \alpha \quad . \tag{7.1}
\]

The \( \mu^R_\alpha \) are defined as the difference between the ground state energies of \( \alpha \) for \( p_\alpha + 1 \) and \( p_\alpha \) electrons in the presence of \( v_R \),

\[
\mu^R_\alpha = E^R_\alpha(p_\alpha + 1) - E^R_\alpha(p_\alpha) \quad , \tag{7.2}
\]

and similarly for \( \mu_M \)

\[
\mu_M = E_M(N_M) - E_M(N_M - 1) \quad . \tag{7.3}
\]

In our simple example, \( \mu_M \) is given in Eq.\( (2.8) \). The relevant value of \( p_\alpha \) is zero, so that \( \mu^R_\alpha \) is just \( E^R_\alpha(1) \), the lowest eigenvalue of

\[
H^R_\alpha = H_\alpha + v_R \quad , \tag{7.4}
\]

with \( H_\alpha \) given by Eq.\( (1.2) \) and \( v_R \) by Eq.\( (6.10) \). The explicit construction of \( v_R \) in Section 6, not possible in general, guarantees that Eq.\( (7.1) \) and therefore electronegativity equalization holds. In the general case, a modification of the Car-Parrinello scheme \([14, 15]\) guarantees electronegativity equalization.

The susceptibility of part \( \alpha \) measures the response of the density of part \( \alpha \) to a small change in the potential \( V_\alpha \) of Eq.\( (6.2) \):

\[
\chi_\alpha(x, x') = -\frac{\delta n_\alpha(x)}{\delta V_\alpha(x')} \quad . \tag{7.5}
\]

For 2 electrons, it is simple to show that

\[
\chi_\alpha(x, x') = -2\psi_\alpha(x)G_\alpha(\mu_M; x, x')\psi_\alpha(x') \quad , \tag{7.6}
\]

where \( G_\alpha(\mu_M; x, x') \) is given by the \( E \to \mu_M \) limit of:

\[
G_\alpha(E; x, x') = G_\alpha(E; x, x') - \frac{\psi_\alpha(x)\psi_\alpha(x')}{E - \mu_M} \quad , \tag{7.7}
\]

and \( G_\alpha \) is the Green’s function for part \( \alpha \):

\[
G_\alpha(E; x, x') = \left[ E - \left( \frac{p^2}{2} + V_\alpha \right) \right]^{-1}(x, x') \quad . \tag{7.8}
\]

Figure 7 shows the susceptibility of the right “atom” for various interatomic separations when the perturbing potential is added at \( x_0 = 3 \) (the numerical calculations were done as described in the Appendix). Electrons flow away from \( x_0 \), building up a peak at \( x_0 \) (positive because of the minus sign in the definition of \( \chi_\alpha \), Eq.\( (7.5) \)), and a negative peak at the closest maximum of the charge density, i.e. at \( a \). With the analytic Green function of an isolated “atom” \([20]\) and Eqs.\( (7.6)-(7.8) \), \( \chi_\alpha \) can be obtained analytically in the large-separation limit:

\[
\chi_\alpha(x, x') = 2e^{-Z|x|} \left\{ e^{-Z|x-x'|} - \left[ \frac{1}{2} + Z(|x| + |x'|) \right] \times e^{-Z(|x|+|x'|)} \right\} e^{-Z|x'|} \quad . \tag{7.9}
\]

We now construct the susceptibility of the whole system, \( \chi_R \), by adding together the susceptibilities of the parts,

\[
\chi_R(x, x') = \sum_\alpha \chi_\alpha(x, x') \quad . \tag{7.10}
\]

The inverse of \( \chi_R \) determines the hardness matrix \( \eta_{\alpha\beta} \) as shown in refs.\([2]\) and \([3]\):

\[
\eta_{\alpha\beta} = \int dx dx' f_\alpha(x) \chi_R^{-1}(x, x') f_\beta(x') \quad , \tag{7.11}
\]

where the Fukui function of part \( \alpha \), \( f_\alpha(x) \),

\[
f_\alpha(x) = \frac{dn_\alpha(N_\alpha, x)}{dn_\alpha} \quad , \tag{7.12}
\]

is simply equal to \( \psi_\alpha^2(x) \) for 2 non-interacting electrons, since \( n_\alpha(N_\alpha, x) = N_\alpha\psi_\alpha^2(x) \) (see also ref.\([10]\)). Thus, we have

\[
\eta_{\alpha\beta} = \int dx dx' \psi_\alpha^2(x) \chi_R^{-1}(x, x') \psi_\beta^2(x') \quad . \tag{7.13}
\]

Figure 8 shows the self-hardness \( \eta_{\alpha\alpha} \) for an isolated H-“atom”, as a function of \( Z \). The constancy of the hardness for large \( Z \) can be understood qualitatively as follows. The inverse susceptibility has units of energy times length squared. When \( Z \) is large, it establishes a length scale inversely proportional to \( Z \), and an energy scale.
proportional to $Z^2$, so the $Z$-dependence cancels out in
the inverse susceptibility. To obtain the hardness, we
multiply $\chi^{-1}$ on the left and right by the Fukui function,
which has the dimension of inverse length. Integrating
over position on the left and right then cancels out the
$Z$-dependence arising from the Fukui functions, and the
result is a $Z$-independent hardness.

8. CONCLUSIONS

Despite the extreme simplicity of the 1D-H2 model
analyzed here – two non-interacting electrons moving
in 1D under the influence of two equivalent attractive
delta-function potentials – that model allows us to illus-
trate the essential features of our partition theory and of
key indices of our chemical reactivity via straightforward
analysis and easy computations.

We have shown that the electron density of the
molecule can be decomposed exactly into a sum of atomic
densities, a rigorous solution of the "atoms-in-molecules"
problem [17].

Electronegativity equalization [18] is built into the par-
tition by the symmetry of the problem, so this homonu-
clear model does not illustrate that principle as well as
a heteronuclear model would. Nevertheless, the current
model does not illustrate that principle as well as
another serious shortcoming of the earlier formulations
of DFT-based CR T is the vanishing of the hardness. W e
have shown explicitly here that the self-hardness, as de-
finite in [3], of an isolated "atom" is positive. Interest-
ably, the hardness saturates as the ionization energy of
the "atom" increases, raising the very interesting ques-
tion of whether such a saturation of hardness with ion-
ization energy exists only over the limited range of
$a$ strong positive correlation between hardness and ion-
ization energy exists in real systems. F or this model,
the "atom" increases, raising the very interesting ques-
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tion of whether such a saturation of hardness with ion-
ization energy exists in real systems. For this model,
a strong positive correlation between hardness and ion-
ization energy exists only over the limited range of $Z$
between 0.4 and 0.7.

KB is supported by NSF CHE-0355405.

APPENDIX: Numerical calculation of the
susceptibility

We first obtained $G_\alpha(E; x, x')$ according to the well-
known prescription [19]:

$$G_\alpha(E; x, x') = 2 \frac{\psi_{\alpha,L}(E, x, x') \psi_{\alpha,R}(E, x, x')}{W[\psi_{\alpha,L}, \psi_{\alpha,R}]} , \quad (A.1)$$

where $x_\alpha = \inf(x, x')$, $x_\alpha = \sup(x, x')$

$$W[\psi_{\alpha,L}; \psi_{\alpha,R}] = \psi_{\alpha,L}(E, x) \psi_{\alpha,R}'(E, x)$$

and the orbitals $\psi_{\alpha,L}$ and $\psi_{\alpha,R}$ are solutions of

$$\left[ \frac{p^2}{2} + V_\alpha(x) \right] \psi_{\alpha,L,R}(E, x) = E \psi_{\alpha,L,R}(E, x) \quad (A.3)$$

satisfying left and right-boundary conditions, respectively:

$$\left| \psi_{\alpha,L}(E, x) \right| \downarrow 0 \quad , \quad x \downarrow -\infty \quad (A.4)$$

$$\left| \psi_{\alpha,R}(E, x) \right| \downarrow 0 \quad , \quad x \uparrow \infty \quad (A.5)$$

The potential $V_\alpha(x)$ of Eq. (A.3) is given by Eq. (6.2), with the reactivity potential $v_R(x)$ of Eq. (6.10). The compu-
tations of $\psi_{\alpha,L,R}(E, x)$ were carried out at $E = \mu_M \pm \Delta E$
with $\Delta E$ chosen for numerical convenience, i.e. large
enough so that $\sup_{x, x'} |G_\alpha(\mu_M \pm \Delta E)|$ does not become
so large as to be inconvenient on the one hand, and small
enough so that $\frac{1}{2} |G_\alpha(\mu_M + \Delta E) + G_\alpha(\mu_M - \Delta E)|$ does
not differ significantly from its limit at $\Delta E \downarrow 0$. We then
calculated $G_\alpha$ of Eq. (7.1) as:

$$G_\alpha(\mu_M; x, x') = \frac{1}{2} \left[ G_\alpha(\mu_M + \Delta E; x, x') + G_\alpha(\mu_M - \Delta E; x, x') \right]$$

$$G_\alpha(\mu_M; x, x') = \frac{1}{2} \left[ G_\alpha(\mu_M + \Delta E; x, x') + G_\alpha(\mu_M - \Delta E; x, x') \right]$$

FIG. 8: Self-hardness vs. $Z$ in the separated-atom limit
(atomic units).
[1] M.H. Cohen and A. Wasserman, Israel J. Chem. 43, 219 (2003).
[2] M.H. Cohen and A. Wasserman, J. Stat. Phys. 125, 1125 (2006).
[3] M.H. Cohen and A. Wasserman, J. Phys. Chem. A 111, 2229 (2007).
[4] P. Hohenberg and W. Kohn, Phys. Rev. 136B, 864 (1964).
[5] W. Kohn and L.J. Sham, Phys. Rev. 140, A1133 (1965).
[6] M. Levy, Proc. Nat. Acad. Sci. USA 76, 6062 (1979).
[7] E.H. Lieb, in Physics as Natural Philosophy, eds. A. Shimony, and H. Feshbach, MIT Press, Cambridge, p.111 (1982).
[8] J.P. Perdew, R.G. Parr, M. Levy, and J.R. Balduz, Jr., Phys. Rev. Lett. 49, 1691 (1982).
[9] J.P. Perdew, in Density Functional Methods in Physics, ed. R.M. Dreizler and J. da Providencia, Plenum, New York, p.265 (1985).
[10] R. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York (1989).
[11] P. Geerlings, F. De Proft, and W. Langenaeker, Chem. Rev. 103, 1793 (2003).
[12] R.G. Parr, R.A. Donnelly, M. Levy, and W.E. Palke, J. Chem. Phys. 68, 3801 (1978).
[13] R.G. Parr and R.G. Pearson, J. Am. Chem. Soc. 105, 7512 (1983).
[14] R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).
[15] M.H. Cohen and R. Car, unpublished.
[16] P. Fuentealba, E. Chamorro, and C. Cárdenas, Int. J. Quant. Chem. 107, 37 (2007).
[17] F.L. Hirshfeld, Theor. Chim. Acta 44, 129 (1977); R. F. W. Bader, Atoms in Molecules - A Quantum Theory, Oxford University Press, Oxford, 1990; R.F. Nalewajski and R.G. Parr, Proc. Natl. Acad. Sci. USA 97, 8879 (2000).
[18] R.T. Sanderson, Science 114, 670 (1951).
[19] G. Arfken, Mathematical Methods for Physicists, Academic Press, New York (1970).
[20] A. Szabo and N.S. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, McGraw-Hill, New York (1989).