

# CANDIDACY REPORT

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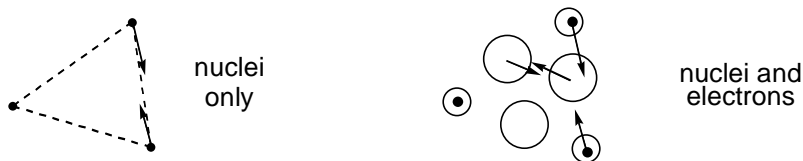
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## Research Report: Hoops, a Semiempirical Floating-Gaussian Reactive Force Field

### Introduction

We would like to develop a fast and general method to simulate organic reactions. Full *ab initio* dynamics is general but not fast; force fields are fast, but not yet general for reactive systems. Reactive force fields attempt to bridge the gap between these two methods by calculating the changes in bonding that occur during the course of a reaction, and modifying force parameters accordingly. The nuclei are treated as classical objects, and in a Born-Oppenheimer framework, the electrons mediate their interaction in some average way. Many complications in this approach arise from the need to derive changes in bonding from the nuclear positions alone, without explicit consideration of individual electron motions.

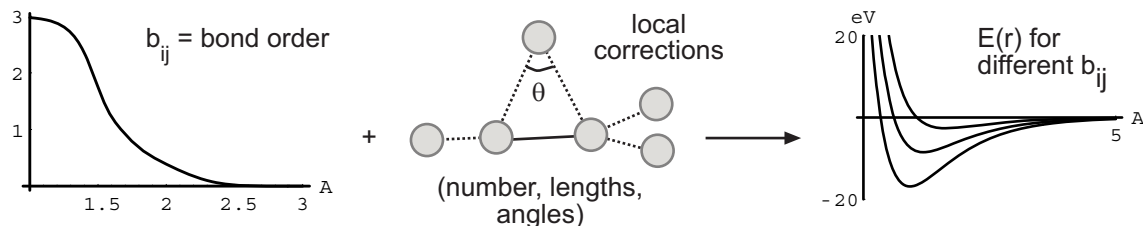
Can the motion of electrons be directly simulated in a force field? Quantum mechanics would at first sight suggest no, with its traditional delocalized picture of electrons in molecular orbitals, whose antisymmetrized product approximates the true electronic wavefunction. But organic chemists drawing reaction mechanisms routinely show electrons moving between molecules in a local fashion, and many approximate QM formulations take advantage of this emergent electron behavior (DFT, GVB).



We propose to develop a force field where the electrons are described as objects with dynamical variables acted on by electrostatic forces, as well as fictitious forces that enforce the Pauli principle. The Hellman-Feynman theorem suggests that once the positions of the electrons are known, classical forces apply; with electrons now semi-classical objects, we will be able to simulate reaction dynamics within a wholly classical force-field framework.

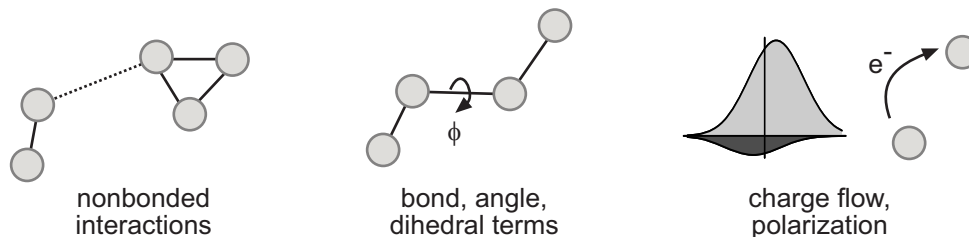
## Previous Work: Reactive Force Fields

The first reactive force fields were developed out of a desire to model covalent bulk systems (silicon, diamond) that were poorly described by simple pair or three-body potentials. Tersoff<sup>1</sup> introduced the idea of a bond-dissociation potential dependent on bond order, which was in turn dependent on bond length and the local coordinating environment:



With this approach, he reproduced bulk silicon energetics, phonon dispersion relations, point defects, and geometric distortions due to surface reconstruction. Brenner<sup>2</sup> extended this model in his REBO potential to correct for conjugation and other nonlocal effects, and added terms to deal with bonds connecting differently coordinating atoms. With this model, he modeled bulk diamond, its surface reconstruction, small molecule surface binding (chemical vapor deposition), and H adsorption.

More recent force fields have added terms designed to allow for the accurate modeling of small molecule reacting species. In his AIREBO force field, Stuart generalized<sup>3</sup> the Brenner potential to include nonbonding and dihedral interactions, and reproduced diamond and graphite bulk structures; pair correlation functions for liquid alkanes, bond enthalpies, bond rotation barriers, and enthalpies of vaporization.



In his ReaxFF<sup>4</sup> and GEEBOD<sup>5</sup> force fields, Goddard took a similar approach, but performed more explicit fits for bond making/breaking over long ranges on an extensive set of QM data, and added an extensive set of screened local potential terms (bonds,

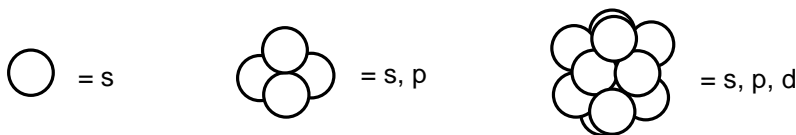
angles, and torsions). A simple charge equilibration model was used to model changes in effective partial charge over the course of reaction; and in a more advanced model, a pair of Gaussian functions was used to represent the overall polarization of atomic core and valence electrons. ReaxFF has successfully reproduced hydrocarbon heats of formation, bond dissociation energies, radical reaction energy surfaces, rotational barriers, and intermolecular interactions. Further extensions<sup>6</sup> have allowed its application to silicon and silicon oxide systems and ferroelectrics (BaTiO<sub>3</sub>).

### Previous Work: Floating Spherical Gaussian Orbitals

The Floating Spherical Gaussian Orbital model, first introduced by Frost<sup>7</sup>, approximates a closed shell system as a Slater determinant of localized Gaussian functions whose positions and extents are allowed to vary:

$$\phi_i(r) \propto e^{-((r-r_i)/\rho_i)^2}$$

The additional variational flexibility of these spherical basis functions allows a minimal set of FSGOs to stand in for a larger set of atom-centered Gaussian-type orbitals with higher angular momentum components<sup>8</sup>:



A Slater determinant of non-orthogonal orbitals has an energy

$$E_{elec} = \sum_{j,k} (j|k) T_{jk} + \sum_{kl,pq} (kl|pq) (2T_{kl} T_{pq} - T_{kq} T_{lp})$$

where

$$T = S^{-1} \quad S_{ij} = \int \phi_i \phi_j d\vec{r}$$

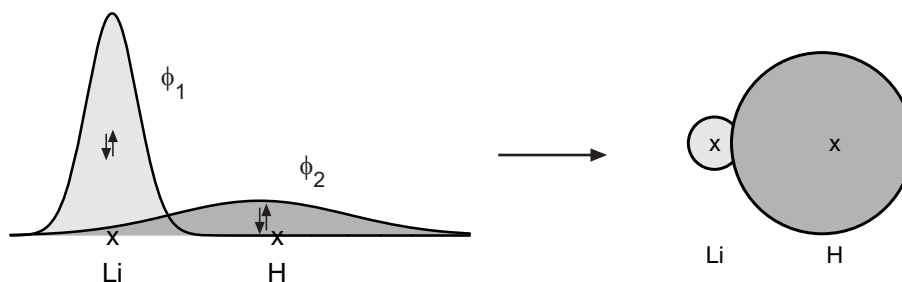
$$(j|k) = \int \phi_j \left( -\frac{1}{2} \nabla^2 - \sum_{nuc} \frac{Z_{nuc}}{r_{nuc}} \right) \phi_k d\vec{r}$$

$$(kl|pq) = \int \phi_k(1) \phi_l(1) r_{12}^{-1} \phi_p(2) \phi_q(2) d\vec{r}_1 d\vec{r}_2$$

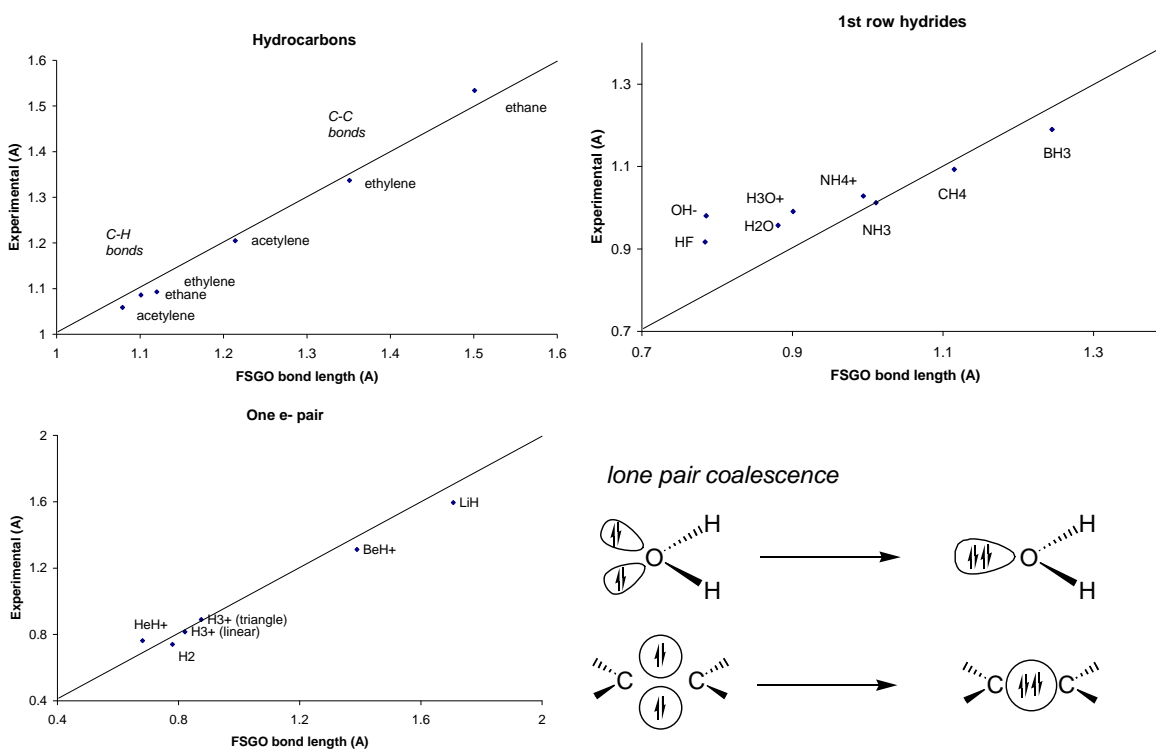
The nuclear positions and electron positions and extents are then varied to minimize the total molecular energy of the molecule ( $E_{elec}$  plus nuclear-nuclear repulsion). Initial

electron positions and extents are assigned based on previously optimized values, or chemical intuition derived from Lewis structures.

FSGO calculations on  $\text{LiH}^{7a}$  reproduced the character of electron localization correctly, the dissociation energy (4%), bond length (7%), and dipole moment (11%).



The bond lengths and angles of several one electron pair molecules<sup>7b</sup>, first row atom hydrides<sup>7c</sup>, and simple hydrocarbons<sup>7d</sup> were found to agree with experimental values quantitatively (within 6%), with two exceptions.



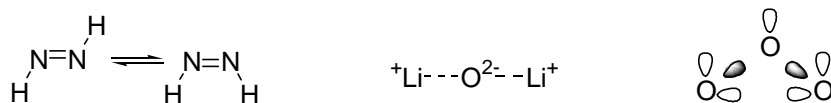
The repulsive potential of  $\text{He}_2$  dimer was also well-reproduced, and when a double-Gaussian modification<sup>9a</sup> was made to the basis set, 96% of the Hartree-Fock energy could be recovered for a series of neutral molecules.

Some difficulties remained however:

1. The bond angles for water ( $87.6^\circ$  vs.  $106.6^\circ$  expt) and ammonia ( $88.4^\circ$  vs.  $104.5^\circ$  expt) were significantly incorrect.
2. Lone pairs and p banana bonds would coalesce to a single center, and were fixed apart at arbitrary distance to prevent the overlap matrix from becoming singular.
3. Rotational barriers for saturated hydrocarbons were consistently too high (5.7 vs. 3.03 kcal/mol expt. for ethane).

Recent improvements in the FSGO scheme have included<sup>9</sup> (1) using double Gaussians or elliptical Gaussians to represent each electron (2) using multiple fixed positive and negative Gaussians to represent lone pairs (3) using pseudopotentials for higher row atoms and (4) allowing different orbitals for different spins, and using projection operators to construct an  $S^2$  eigenstate.

An evaluation<sup>10</sup> of FSGO for isomers of  $N_2H_2$ ,  $Li_2O$ ,  $C_3H_4$ , and  $O_3$  concluded that (1) semiquantitative bonding features involved with cis-trans isomerisation and ionic bonding were well described, (2)  $O_3$  resonance structures were well described, (3) energy differences of isomers with different numbers of multiple bonds were inaccurate, and (4) lone pairs and their effect on bond angles were particularly badly described.



We foreshadow our current project by noting that the original FSGO model and all of its improvements have sought to preserve a key quality: the method is completely *ab initio*, with no adjustable parameters. A downside of this quality, though, is that no parameters are available to compensate for the incomplete description of the system due to the subminimal basis set used. In our work, we have taken a step back, and have extracted from the FSGO formalism a deformation function that describes how electrons interact with each other and the nuclei. This function can be generalized with adjustable parameters, and some room is thus allowed to modify the interactions based on empirical rules to obtain more accurate results.



### **A Note on FSGO vs. HF/SCF Efficiency**

It is useful to pinpoint particular simplifications the FSGO method provides over a conventional HF/SCF algorithm:

1. Density matrix is identity. No self-consistent iteration of a density matrix is needed.
2. All integrals contain only products of *s* type Gaussian functions.
3. Minimal number of basis functions used.
4. Can minimize electronic and nuclear variables together, rather than in separate stages.

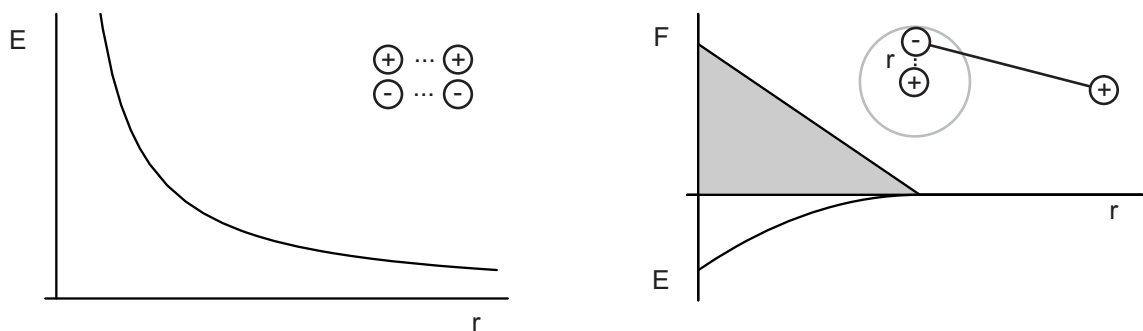
On the other hand,

1. Optimization of electron positions and extents is equivalent to SCF iterations, and does not necessarily converge faster.
2. Inversion of the overlap matrix still required (conceptually the same as diagonalization and symmetric orthogonalization of basis functions).
3. Calculation and storage of all possible four-center two-electron integrals still required.

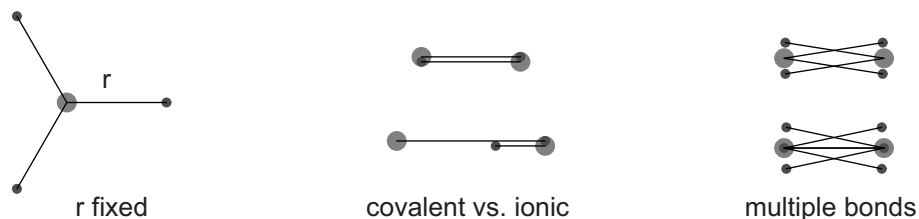
As (3) is the bottleneck in most *ab initio* calculations on moderate sized molecules, we expect time savings to arise primarily from a reduction in the number of basis functions needed to describe a given system. FSGO results may also be easier to interpret, as the underlying model corresponds closely to intuitive notions of electron localization and chemical bonding.

### **Koosh: A Minimal Model of Electrons in Molecules**

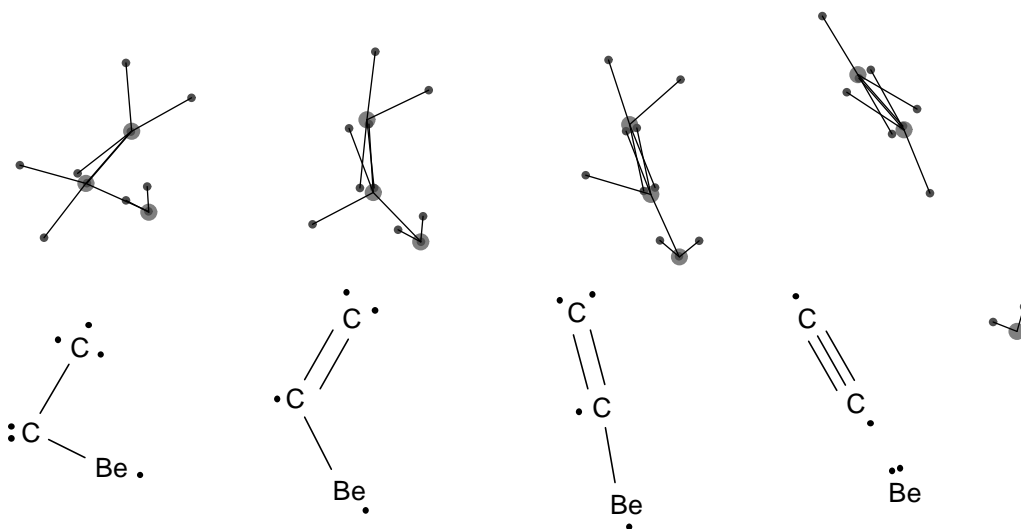
In starting our project, we initially wondered: what is the simplest electron model that will reproduce qualitative aspects of reaction mechanisms? These thoughts inspired Koosh, a model where electrons are represented as point charges constrained to move a fixed distance away from the nucleus. Electrons repel each other according to Coulomb's law, as do nuclei; but when an electron attached to one nucleus approaches another, the attractive force increases linearly with closeness to the other nucleus. Thus we have a model that should account for (1) electrons wishing to occupy fixed orbitals (2) penetration and (3) screening effects.



Atomic coordination geometries change naturally as neighboring atoms approach, with VESPR rules are enforced by the mutual repulsion of the electrons. Each atom has a defined radius and electronegativity, and bonding is strongest between atoms of similar radii. Atoms of different radii are forced to form “ionic” bonds where the electron pair is closer to one nucleus than the other. Multiple bonds may also be formed, and the resultant hybridizations ( $sp$ ,  $sp^2$ ,  $sp^3$ ) are consistent with previous expectations.



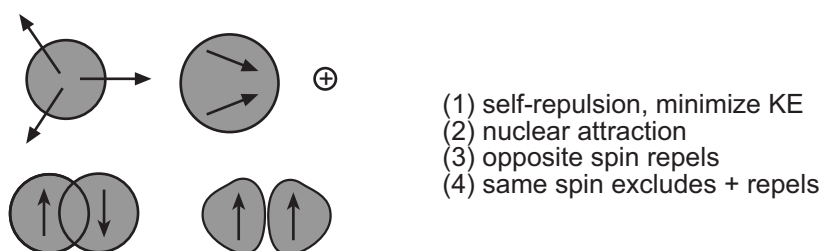
This “toy model” can also reproduce qualitative aspects of bond breaking and forming. Below we show a beryllium atom bound to a 2C cluster, which forms a  $C\equiv C$  triple bond with expulsion of beryllium.



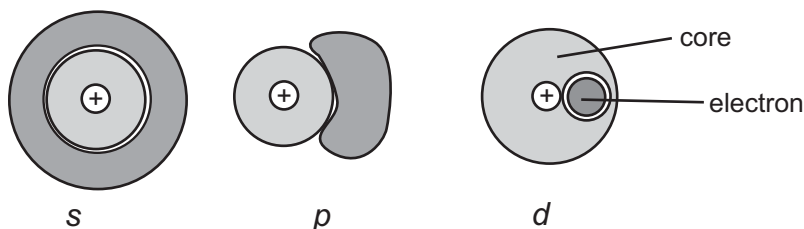
However, the model's generality is clearly limited, as (1) all bond lengths are predetermined, (2) electrons have no extent and cannot polarize, (3) electrons have no spin and repel more weakly than they should from the Pauli principle, and (4) heterolytic cleavage of bonds is impossible, as each electron is permanently associated with a single atom. These issues are addressed in our next model.

### The Excluding Charged Drop Picture

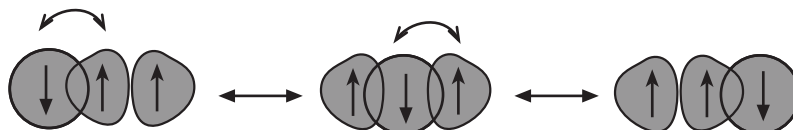
From one extreme to another: what model of an electron most meaningfully represents its localization in a molecule? Electrons expand to minimize kinetic energy and contract around nuclei to minimize potential energy, much as a charged drop seeking to minimize surface tension would. Opposite spin electrons repel each other; same spin electrons do as well, but must obey the Pauli principle, so they exclude each other too:



Consider three possibilities created by adding an electron to a neutral core: (1) the electron may wrap itself entirely around the core (*s-like*), (2) the electron may wrap itself partially around the core (*p-like*), or (3) the electron may burrow inside the core (*d-like*). Further calculation is required to determine the preferred mode of addition.

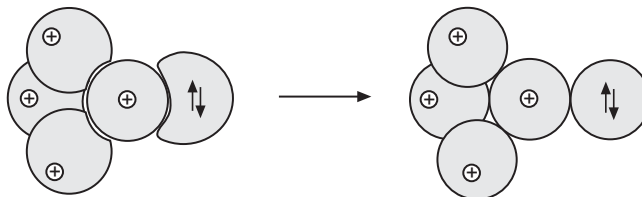


We also assume that opposite spin electrons exchange rapidly with each other with a rate that increases with increasing electron overlap. This completes our intuitive picture; we now seek a model that can approximate roughly these presumed realities.

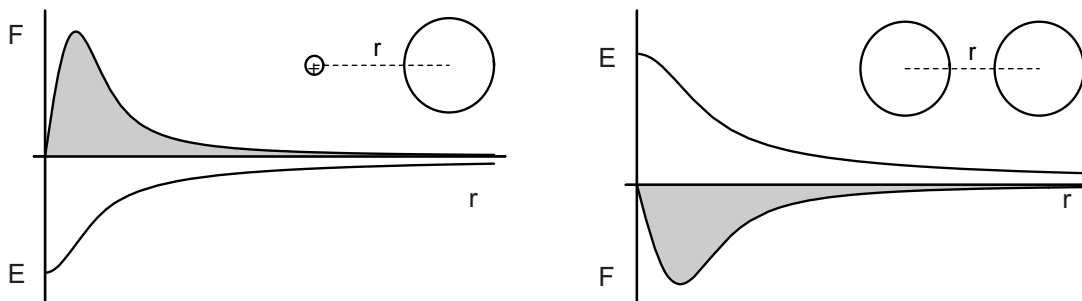


### First Generation Hoops: Rigidly Deforming Electrons

Consider a molecule of ammonia. Our intuition would suggest that each set of bonding electrons would have a complex shape determined by an interplay of nuclear attractions, electron repulsions, and same spin exclusion. The electron density could be shifted toward one portion of the electron too, complicating the energy calculations.



We turn to a simpler model. The electrons are taken to be rigid spherical Gaussian functions with a kinetic energy given by  $(1/2)\int \nabla^2 \psi dV$ . The electrostatic interactions are straightforward to calculate, and result in screened Coulomb potentials:



Same spin electrons are assumed to rigidly deform in response to each other, leading to a *deformation energy* that gives rise to a fictitious *Pauli force*. Improvements in this model will later center on this term, which not only describes how same spin electrons repel, but also how they change their shape to exclude each other. The final energy expressions are shown below ( $r_1, r_2$  are electron radii;  $r$  is the electron-electron or electron-nuclear distance;  $c$  is large enough to prevent same-spin electron incursion during a time step.)

$$E_{KE} = \frac{3}{2} \frac{1}{r_1^2}$$

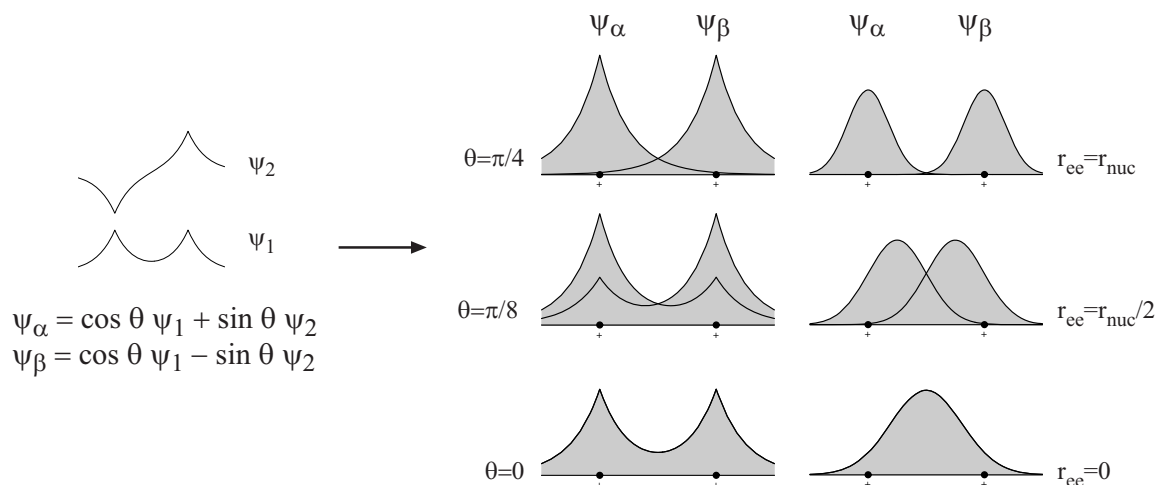
$$E_{elec-nuc} = -\frac{Z_c}{r} \text{Erf} \left( \sqrt{2} \frac{r}{r_1} \right) \quad E_{nuc-nuc} = \frac{1}{r}$$

$$E_{deform} = \begin{cases} c\Delta & \text{if } \Delta = (r_1 + r_2) - r > 0 \\ 0 & \text{otherwise} \end{cases}$$

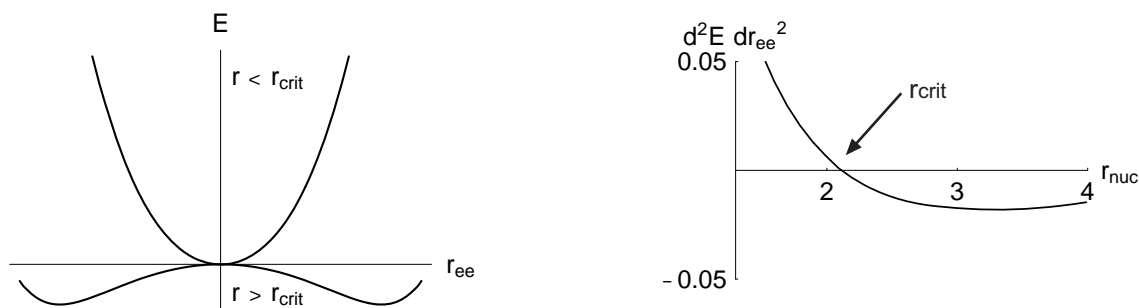
$$E_{elec-elec} = \frac{1}{r} \text{Erf} \left( \sqrt{2} \frac{r}{\sqrt{r_1^2 + r_2^2}} \right)$$

## Results: Homolytic Dissociation of H<sub>2</sub>

Ideally, electrons would be localized correctly in bonds for all bond distances. As a test case, we examined H<sub>2</sub>, which in dissociating moves from a closed-shell system best described by a restricted wavefunction to an open-shell system best described by an unrestricted wave function. In the LCAO-HF picture, non-symmetry constrained unrestricted orbitals can be written as a linear combination of atom-centered orbitals. In the floating orbital picture, the analogous linear combination is formed simply by allowing electrons to move off-center from the nuclei:

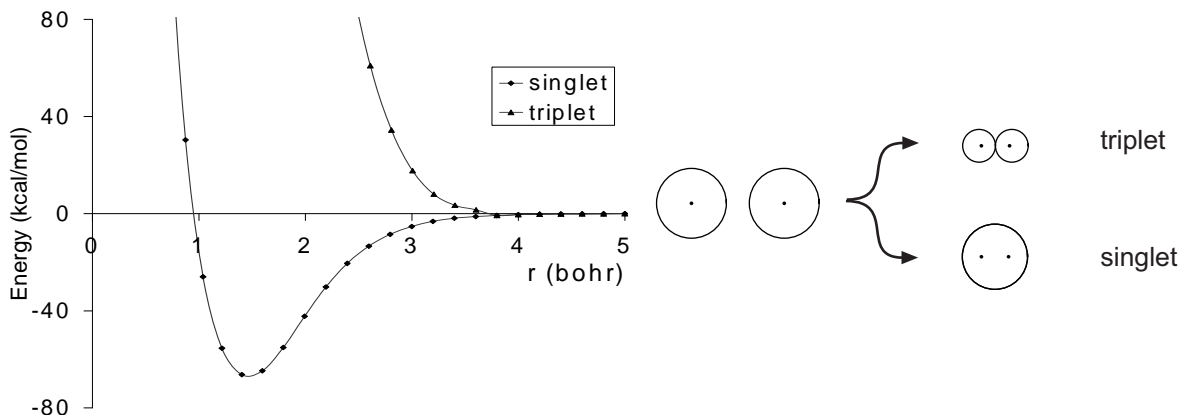


We observe that below a critical nuclear separation, the restricted wavefunction is only the only stable solution – the electrons occupy the same space. Above  $r_{crit}$ , that solution becomes unstable, and electrons become localized on individual atoms. In our model,  $r_{crit}$  is 2.13 bohr (2.3, UHF).



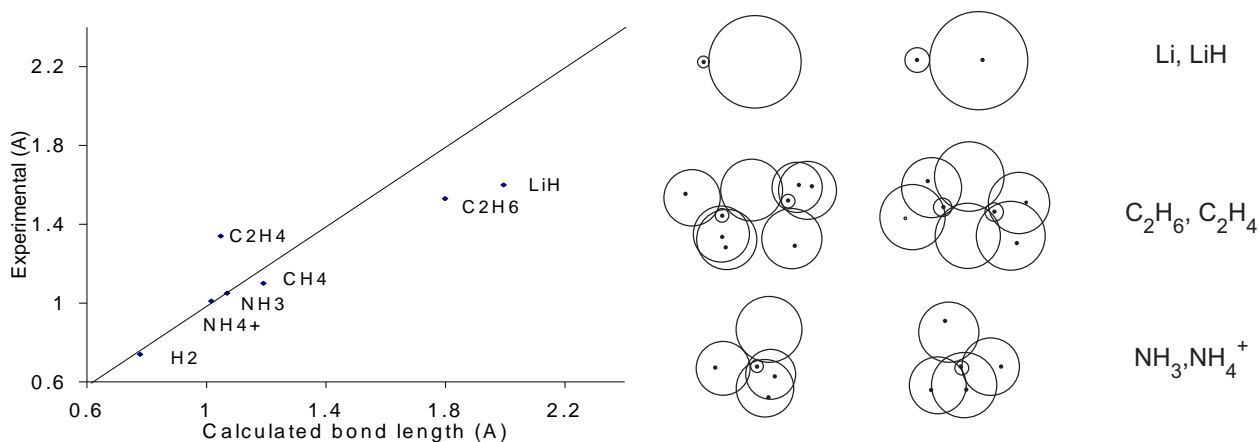
We change the nuclear separation while optimizing the electron positions and extents, allowing the system to make a continuous transition between a restricted form at short distances and an unrestricted form at long distances. Our wavefunction will suffer from triplet contamination at these longer distances, which may be alleviated by allowing spin-

exchange. The equilibrium bond distance calculated for  $H_2$  is 1.47 bohr (1.40), close to experimental, but the dissociation energy of 67.2 kcal/mol (109.5) is certainly too low. We also calculate the triplet binding curve, whose repulsive portion is a direct consequence of the increased kinetic energy from electron deformation as the nuclei are brought together.



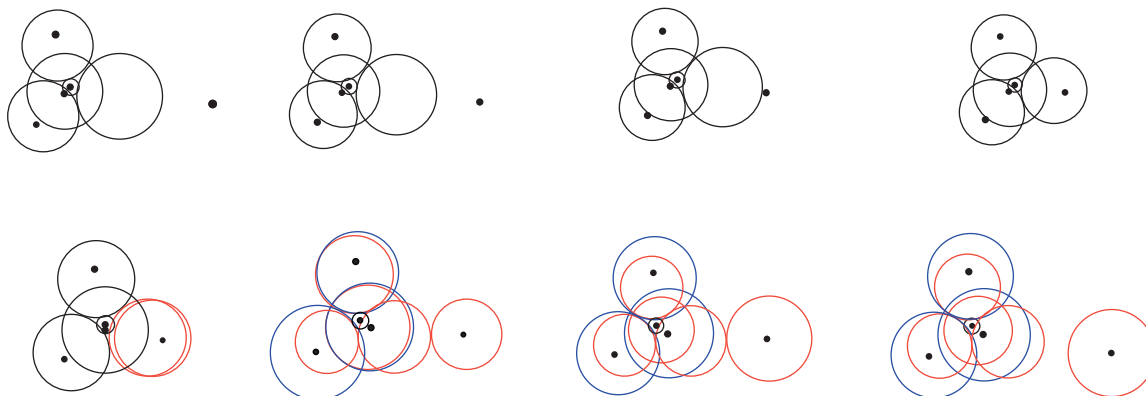
### Results: First Row Hydrides and Simple Hydrocarbons

To our surprise and delight, larger systems were also stable, with bond lengths and angles comparable to experimental values. Some features remained difficult to describe: (1) carbon-carbon single bonds were bent, presumably from the lack of any long-range character to our deformation function (2) double bonds formed via a pair of “banana” bonds and were significantly too short.



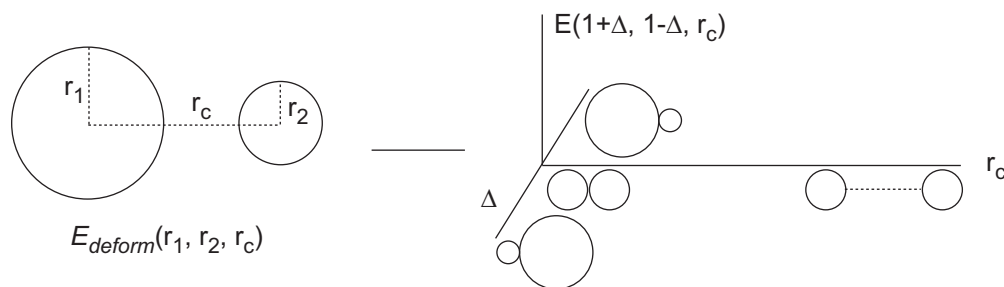
We also performed some simple trajectory calculations, taking the electrons to be half the mass of a proton, and allowing the electron positions and extents to change along with the nuclear coordinates. For the first reaction, we looked at the protonation of ammonia; for

the second reaction, we looked at the homolytic bond cleavage of  $\text{CH}_4$  upon excitation of one of its bonds to the triplet state. In the first case, all electrons remained spin-paired, while in the second case, a  $\text{CH}_3$  radical was formed, and the electrons with spin opposite that of the radical electron expanded outward slightly. Both results were consistent with our chemical expectations.



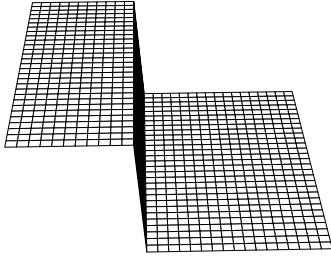
### Toward a Better Deformation Function

The deformation function describes the nonelectrostatic interaction of same-spin electrons, and is analogous to the exchange-correlation functional in the Kohn-Sham formulation of density functional theory. A simple hard-sphere function **1** performs adequately, particularly if additional scaling factors were included, but fails to realistically describe multiple bonding, long range interactions, and  $s$  electrons (one electron inside another). Thus over the next few months, we sought to improve our deformation function.



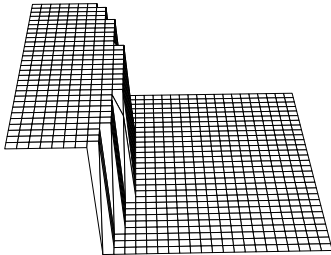
Below we show the deformation functions evaluated (**1-6**) and rejected, as well as the ones currently in use (**VB1-3**). We have plotted our functions in a form that emphasize three key properties: (1) long-range behavior, (2) response to changes in the relative size of the electrons  $\Delta$ , and (3) behavior at the coalescence limit ( $r_1=r_2, r \rightarrow 0$ ).

1

**hard sphere**

$$E_{deform} = \begin{cases} c\Delta & \text{if } \Delta = (r_1 + r_2) - r > 0 \\ 0 & \text{otherwise} \end{cases}$$

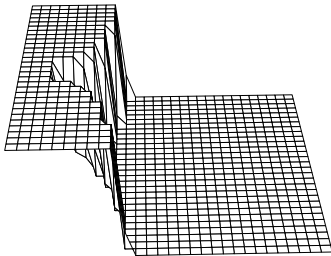
2

**hard sphere with effective radius**

$$\Delta = R_{eff}(r_1) + R_{eff}(r_2) - r$$

$$R_{eff}(r) = r \sqrt{\log\left(\frac{1}{t}\right) - \frac{3}{2} \log\left(\sqrt{\frac{\pi}{2}} r\right)}, \quad t = 0.4$$

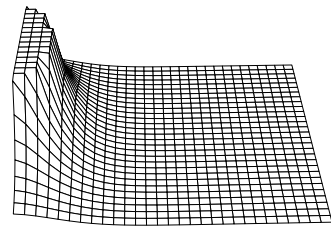
3

**hard sphere with exchange stabilization**

$$\Delta = (r_1 + r_2)(1 - \rho E_{exch}) - r$$

$$E_{exch} = \frac{\sqrt{2}\pi}{r_1^{-2} + r_2^{-2}} e^{-\frac{r}{r_1^2 + r_2^2}}, \quad \rho = 0.37$$

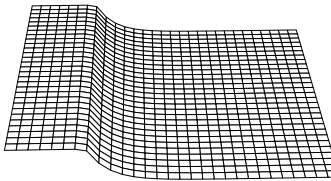
4

**overlap based functions**

$$E_{deform} = \frac{S^2}{1 - \beta S^2}$$

$$S = \left( \frac{2}{r_2/r_1 + r_1/r_2} \right)^{3/2} e^{-\frac{r^2}{r_1^2 + r_2^2}}, \quad \beta = 1$$

5

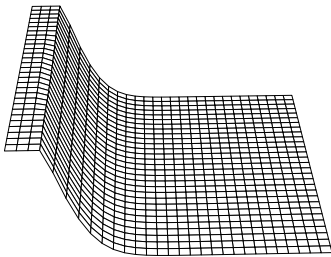
**fit to He<sub>2</sub> dimer**

$$E_{deform} = a(r)(r_1 + r_2) + b(r)$$

$$a(r) = 44.523e^{-3.305r} + 1.669$$

$$b(r) = 60.476e^{-2.926r} + 3.800$$

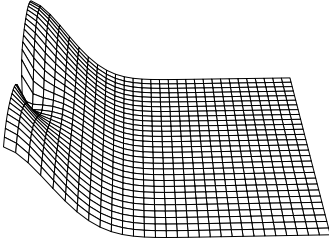
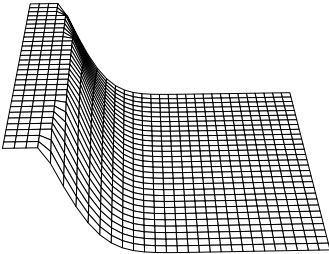
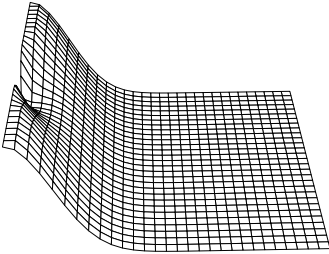
6

**generic deformation function**

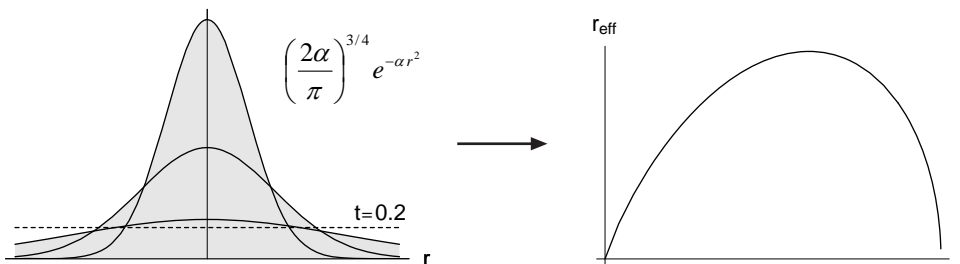
$$E_{deform} = m e^{-\frac{4cr^2}{r_1^2 + r_2^2}} \left( 1 + k(r_1 - r_2)^2 \right)$$

$$m = 3.0, k = 0.1, c = 1.2$$



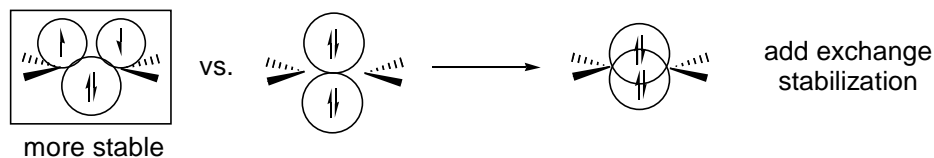
VB1		<p><b>valence-bond based function</b></p> $E_{deform} = \left( 3 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - 4 \left( \frac{3(r_1^2 + r_2^2) - 4r^2}{(r_1^2 + r_2^2)^2} \right) \right) \cdot \frac{S^2}{1 - S^4}$ <p><math>\alpha(r \text{ scaling}) = 1.3, \beta(r_1, r_2 \text{ scaling}) = 1.1</math></p>
VB2		<p><b>valence-bond based, singularity removed</b></p> $E_{deform} = \left( 3 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - 4 \left( \frac{3(r_1^2 + r_2^2) - 2r^2}{(r_1^2 + r_2^2)^2} \right) \right) \cdot \frac{S^2}{1 - S^4}$ <p><math>\alpha = 1.02, \beta = 0.8, s(\text{Coulomb screening}) = 0.9</math></p>
VB3		<p><b>valence-bond based, 2e<sup>-</sup> included</b></p> $E_{deform} = \left( 3 \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - 4 \left( \frac{3(r_1^2 + r_2^2) - 4r^2}{(r_1^2 + r_2^2)^2} \right) + \frac{2}{r} \left( \text{Erf} \left( \frac{\sqrt{2}sr}{\sqrt{r_1^2 + r_2^2}} \right) - \text{Erf} \left( \frac{sr}{\sqrt{2}} \sqrt{\frac{1}{r_1^2} + \frac{1}{r_2^2}} \right) \right) \right) \cdot \frac{S^2}{1 - S^4}$ <p><math>\alpha = 1.1, \beta = 0.9, s = 0.97</math></p>

Function **2** added an effective radius function to the hard-sphere description which comes from taking a fixed threshold and measuring the intercept of a normalized Gaussian function at that threshold.  $R_{eff}$  decreases after a critical radius, which is physically meaningful, as it implies that over a certain size, electrons will allow other electrons to “burrow” inside with only minimal local deformations. Unfortunately **2** did not solve any problems associated with **1**.

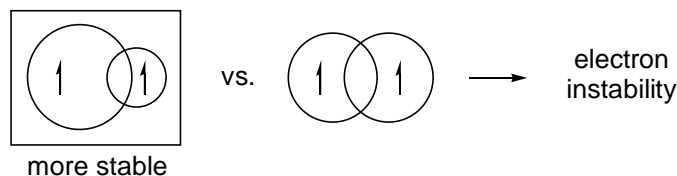


Function **3** was derived to address a specific problem: alkene banana bonds were unstable and would split into a singlet diradical. Adding a fractional exchange stabilization into the potential caused instabilities, but decreasing  $R_{eff}$  by an amount proportional to

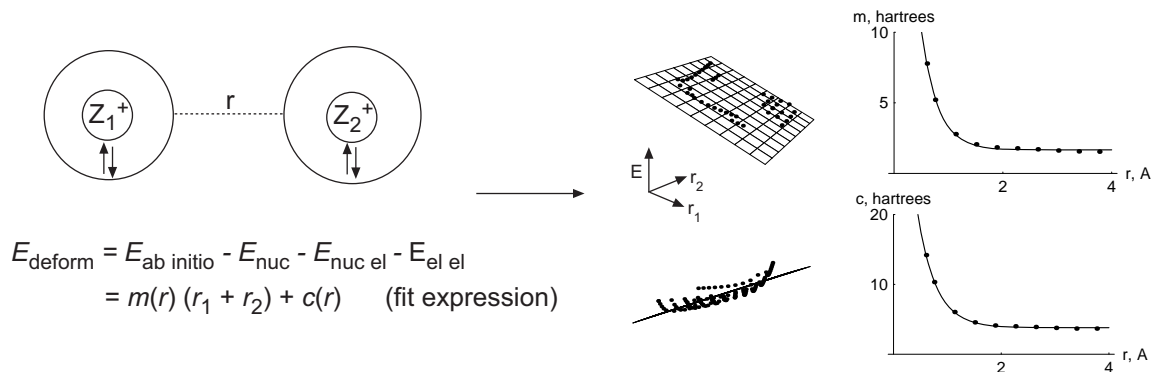
exchange stabilization successfully restabilized banana bonds by allowing adjacent lone pairs to move more closely together. Unfortunately, the procedure failed catastrophically for some cases (adjacent H atoms in ethane, LiH unstable). Scaling electron charges based on overlap, scaling kinetic energy, and using double Gaussians also failed to improve matters.



We experimented with using functions solely dependent on the overlap  $S$  on grounds that they would be more physically meaningful, but as shown in **4**, dissimilar electron sizes overlap less, and so more stably interact, which immediately led to electron size instabilities in our molecules.



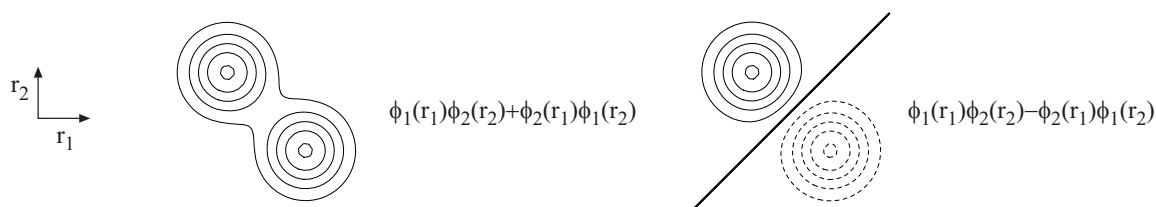
Next, we calculated *ab initio* energies (Huzinaga 10s He basis set, RHF) of He<sub>2</sub>-like atoms with fractional charges, thus allowing examination of a wide range of electron sizes. After fitting the *ab initio* charge densities to Gaussian functions and subtracting out all the electrostatic energy components, we were left with a deformation function, which we fit to a function of  $r$  and  $r_1+r_2$ . Sadly, problems with the reference energies, as well as inadequate knowledge of a proper functional fit form, led to a function **5** that performed even worse than the original hard-sphere function.



Finally, we tried combining the best attributes of our previous functions into a single generic deformation function with multiple parameters. Function **6** multiplied the  $r$  dependence of the overlap  $S$  by a term that stabilized similar electron sizes. While the first row hydrides were accurately described by this function,  $\text{H}_3\text{C}-\text{CH}_3$  was too long and  $\text{LiH}$  was too short, implying that the function's dependence on  $r_1-r_2$  was still incorrect.

### The Valence Bond Deformation Functions

At this point, we were in desperate need of a functional form based on principles more rigorous than intuition and less system-specific than *ab initio* data. We turned to Professor Goddard's notes (2.1.5, 2.3.4b, (1986) Chemistry 120), which contained a valence bond analysis of bonding in  $\text{H}_2$ . The analysis suggested that the energy difference between the bonding and antibonding states of  $\text{H}_2$  arose *primarily* from the difference in the *kinetic energies* of symmetric and antisymmetric wavefunctions.



We decided to define  $\Delta E_{deform}$  as exactly this difference (VB exchange energies):

$$\begin{aligned} \Delta E_{deform} &= \frac{\langle 12-21 | \hat{H} | 12-21 \rangle}{\langle 12-21 | 12-21 \rangle} - \frac{\langle 12+21 | \hat{H} | 12+21 \rangle}{\langle 12+21 | 12+21 \rangle} \\ &= \frac{2\langle 12 | \hat{H} | 12-21 \rangle}{2-2S^2} - \frac{2\langle 12 | \hat{H} | 12+21 \rangle}{2+2S^2} \\ &= \frac{1}{1-S^2} (\langle 12 | \hat{H} | 12 \rangle - \langle 12 | \hat{H} | 21 \rangle) - \frac{1}{1+S^2} (\langle 12 | \hat{H} | 12 \rangle + \langle 12 | \hat{H} | 21 \rangle) \\ &= \frac{1}{1-S^4} (2S^2 \langle 12 | \hat{H} | 12 \rangle - 2\langle 12 | \hat{H} | 21 \rangle) \end{aligned}$$

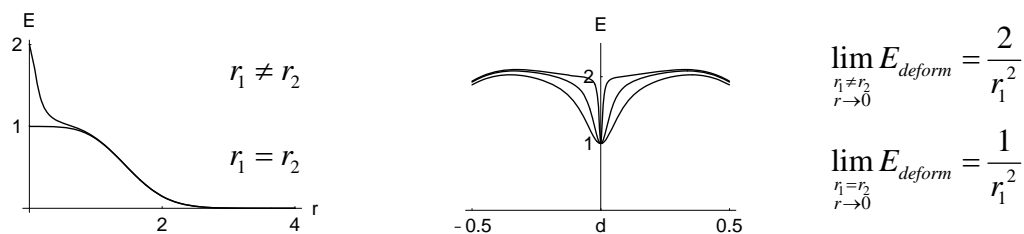
Since  $H = (t_1 + V_1) + (t_2 + V_2) + 1/r_{12}$ , we can split  $\Delta E_{deform}$  into kinetic energy, potential energy, and  $1/r_{12}$  components:

$$\begin{aligned} \Delta E_{KE} &= \frac{1}{1-S^4} (2S^2(t_{11} + t_{22}) - 2S(t_{12} + t_{21})) \\ \Delta E_{PE} &= \frac{1}{1-S^4} (2S^2(V_{11} + V_{22}) - 2S(V_{12} + V_{21})) \\ \Delta E_{1/r_{12}} &= \frac{1}{1-S^4} (2S^2 J_{12} - 2K_{12}) \end{aligned}$$

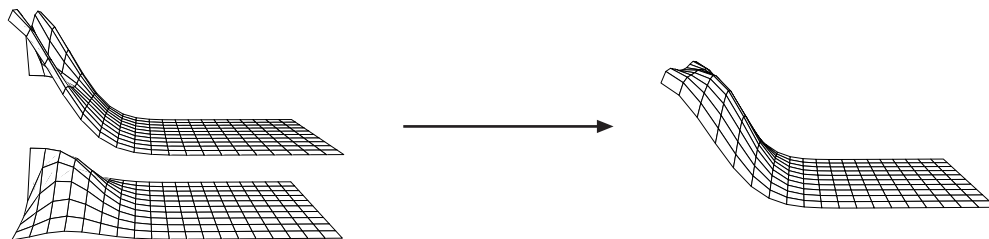
**VB1** was derived by taking  $\Delta E_{deform} = \Delta E_{ke}$ , making use of the following expressions:

$$t_{11} = \frac{3}{2} \frac{1}{r_1^2} \quad t_{22} = \frac{3}{2} \frac{1}{r_2^2} \quad t_{12} = t_{21} = S \left( \frac{3}{r_1^2 + r_2^2} - \frac{2r^2}{(r_1^2 + r_2^2)^2} \right)$$

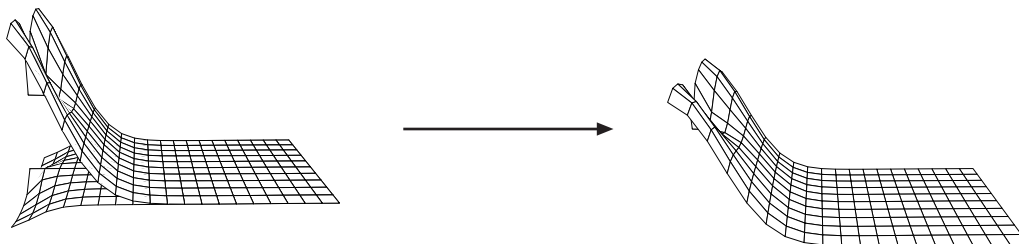
This function gave good results, particularly when the scaling factors  $\alpha$  and  $\beta$  were used on  $r_1$ ,  $r_2$  and  $r$  respectively. **VB1** contains a singularity at  $r_1=r_2$  when  $r=0$ , which is not necessarily harmful, as it corresponds to a regime that should not be accessible to two same-spin electrons:



However, multiple bonds exert a large driving force toward  $p$  electron coalescence, and this particular singularity caused “glitches” in the minimization process. **VB2** fixed this problem by arbitrarily removing the offending singular component of the expression:



This removal was not entirely satisfactory from a physical standpoint, and we found that by instead adding in the  $\Delta E_{1/r12}$  two-electron term, we could remove enough of the singularity to resolve the multiple bonding glitches and avoid lone pair coalescence. The resulting function was named **VB3**.





## Modification of the VB1 Deformation Function

The VB series deformation functions produce lone pairs that are somewhat unstable on nitrogen and even more unstable on oxygen. To remedy this defect, we added an exchange interaction between opposite spin electrons that prevents lone pairs from separating into open shells:

$$\Delta E_{exch}^g = \frac{S^2}{1-S^2} \cdot \left( \frac{3}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - 2 \left( \frac{3(r_1^2 + r_2^2) - 4r^2}{(r_1^2 + r_2^2)^2} \right) \right)$$

$$\Delta E_{exch}^u = \frac{-S^2}{1+S^2} \cdot \left( \frac{3}{2} \left( \frac{1}{r_1^2} + \frac{1}{r_2^2} \right) - 2 \left( \frac{3(r_1^2 + r_2^2) - 4r^2}{(r_1^2 + r_2^2)^2} \right) \right)$$

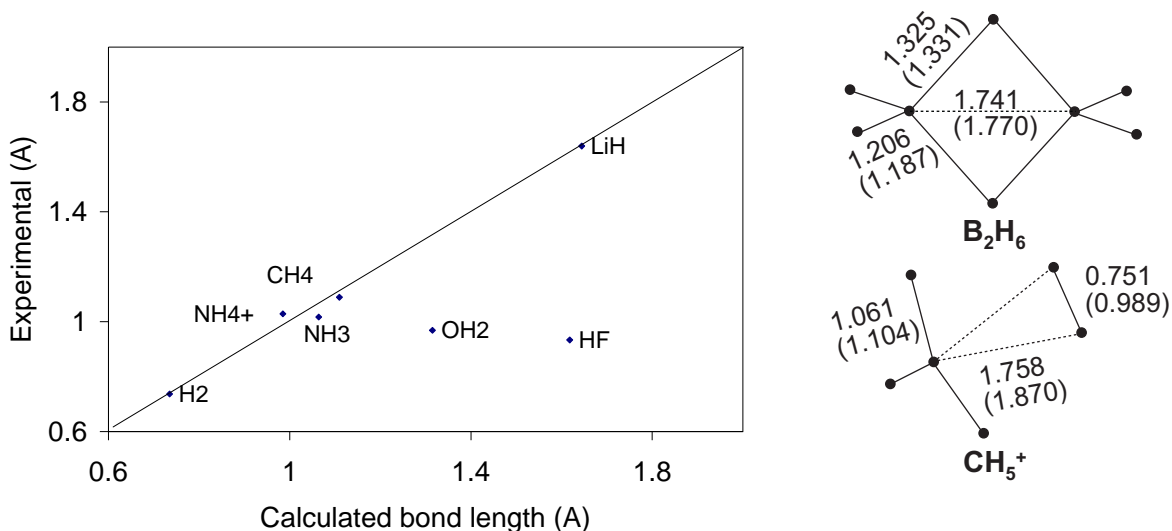
$$\Delta E_{deform}^{\uparrow\uparrow} = \Delta E_{exch}^u + (1-\rho) \Delta E_{exch}^g$$

$$\Delta E_{deform}^{\uparrow\downarrow} = \rho \Delta E_{exch}^g$$

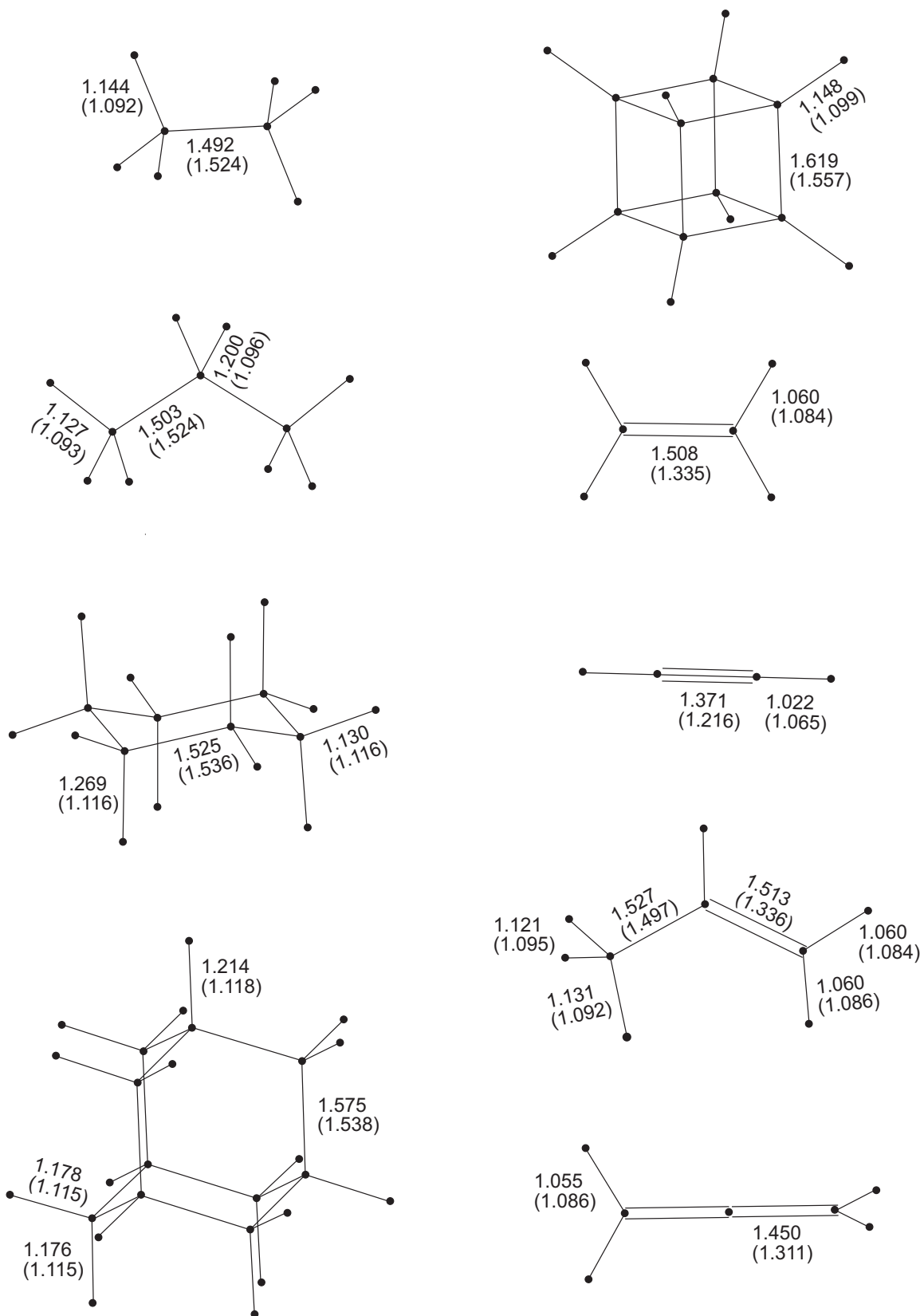
This modified function **VB1'** was used with the parameters  $s = 0.97$ ,  $\alpha = 1.125$ ,  $\beta = 0.9$ , and  $\rho = -0.2$  to derive the results below.

## First Row Hydrides and Hydrocarbons

We find that molecules without lone pairs – protonated amines, boron hydrides, and even  $\text{CH}_5^+$  – have the correct bond lengths and angles. Lone pairs, particularly those on more electronegative atoms, are stable but are not well-described, and cause severe distortions away from an ideal geometry.



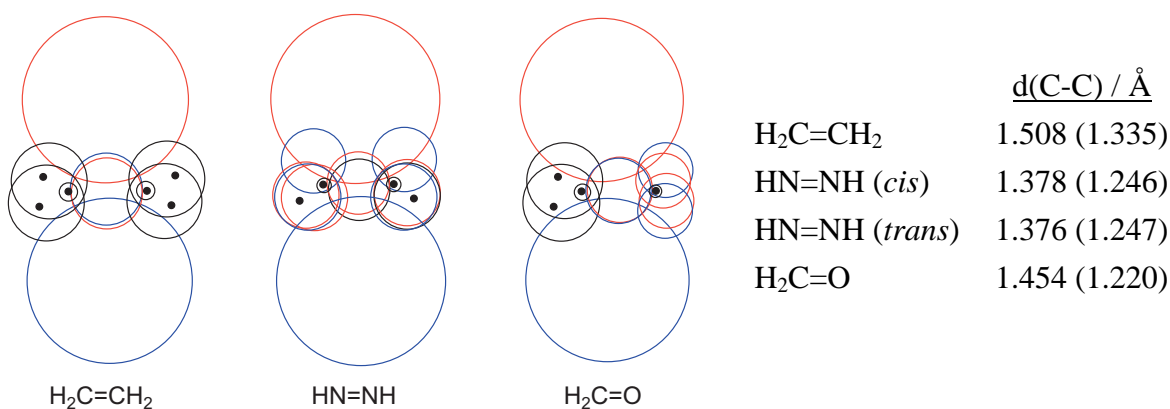
Hydrocarbons show the correct hybridizations and bonding geometries, and the bond angles are quite good. However, (1) axial bonds are too long relative to equatorial bonds, so that cyclohexane will tend to isomerize to benzene + 3H<sub>2</sub>; (2) double and triple bonds



are too long (although the usual floating Gaussian difficulty of multiple bond coalescence is not observed, perhaps a consequence of the different orbitals for different spins representation); and (3) propene shows too much resonance, so that its single and double bonds are almost identical in length. Sigma-pi type bonding is preferred over banana-type bonding in the VB1 model by 166 kcal/mol for double bonds and 125 kcal/mol for triple bonds. Finally, the rotational barrier of ethane is found to be 2.1 (3.0) kcal/mol, and the bond dissociation energy of ethane is found to be 140.4 (80) kcal/mol.

### Heteroatoms and Multiple Bonding

Formaldehyde differs from ethylene by the presence of a higher nuclear charge, which serves to contract and polarize the double bond; and by its lone pairs, which is sufficiently distant to the CH<sub>2</sub> group that the HCH bond angle remains unchanged. These observations are consistent with our calculations; the HCH bond angle for ethylene is 119.7° (121.7°) and for formaldehyde is 119.0° (122.2°). The floating  $\pi$  orbitals in formaldehyde appear to be pushed toward the carbonyl carbon by the oxygen lone pair, which runs counter to our expectation that it should be polarized toward oxygen. Ultimately the relative electrophilicities of the two sites may derive from interactions with orbitals other than the  $\pi$  orbitals.



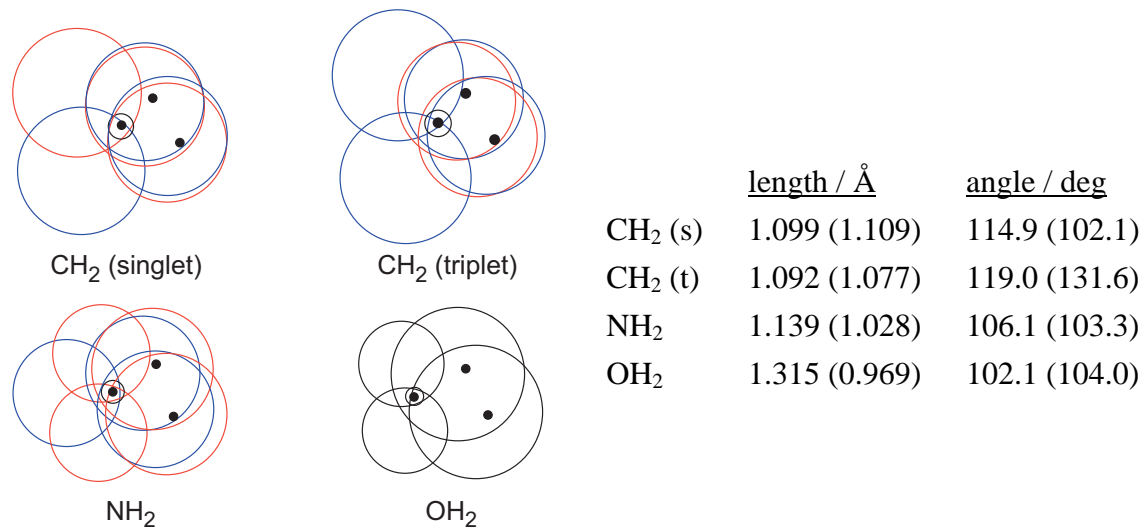
Both *cis*- and *trans*-diimide show unexpected behavior in our model: the nitrogen holds its lone pairs loosely enough that a single electron from each lone pair jumps to the N-H bond (0.972 Å (1.033)). This does not change the N-H bond distance significantly, but reduces the steric interactions between the lone pairs, so that the N=N double bond is too



short. The electron transfer has no chemical rationale and so must be regarded as a deficiency in the current VB1' model.

### Carbenes and the Singlet-Triplet Gap

This section was difficult to write, as the cases presented here are clearly treated poorly with our current model. CH<sub>2</sub> triplet was predicted to have a higher bond angle than CH<sub>2</sub> singlet, in our description because the free-electron pair of the singlet lies more in the plane than the free-electron pair of the triplet. However, the difference in angle (5°) is significantly less than the observed difference in angle (29°). Also, the singlet-triplet splitting is 50.2 kcal/mol in the *wrong direction* (vs. 8.5 kcal/mol expt). This may arise from two factors: (1) **VB1'** does not currently include the decrease in electron repulsion caused when two same-spin electrons interact with each other ( $\Delta E_{1/r_{12}}$ ), which is absolutely key in calculating an accurate singlet-triplet splitting energy; and (2) the fractional ground exchange energy included in **VB1'** may improve lone pair stability at the expense of accurate open shell energetics.



As the nuclear charge increases in the CH<sub>2</sub> to NH<sub>2</sub> to OH<sub>2</sub> series, the bond lengths are expected to decrease. Instead, in our case, the lone pairs contract inward enough to push the bonds outward and *increase* the bond lengths. This has the side effect of decreasing the steric repulsion between hydrogens, so that the bond angle *decreases*, instead of increasing slightly as observed experimentally. This trend would appear to suggest that our lone pairs, particularly when small, repel other electrons too strongly.

## Conclusions

We have developed Hoops, a reactive force field that explicitly describes electron dynamics via a semiempirical floating Gaussian representation. The electrons interact with the nuclei and each other purely electrostatically, with a deformation function added to enforce Pauli exclusion of same spin electrons and to partially correct for deficiencies in the floating Gaussian basis. An early version of the method using a hard sphere deformation function predicted a variety of small organic molecule geometries correctly. More recent models use a valence-bond derived deformation function that accounts for the change in kinetic energy upon electron orthogonalization, with modifications to stabilize lone pairs (which are traditionally described poorly with floating Gaussians). We obtain good geometries for first row hydrides and hydrocarbons, but our model fails to predict the bonding in diimide, and completely fails to predict the singlet-triplet splitting in  $:\text{CH}_2$  and related geometry trends. Future work will focus on improving the deformation function with an emphasis toward better describing lone pairs, and possibly extending the basis functions to a more variationally flexible form.

## Acknowledgements

I would like to thank Professor Goddard for providing me with direction on this project through some wonderful discussions on chemical bonding, approximate techniques, and the historical development of key methodologies, as well as some very specific and practical suggestions. He has also allowed me to spend a significant amount of time working on a riskier-than-average project. Alejandro Strachan kindly took the time to discuss with me the algorithms behind and implementations of current reactive force fields, and I would like to thank him as well.

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