

Questioning the orbital picture of magnetic spin coupling: a real space alternative

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Abstract

The prevailing magnetic spin coupling paradigm is based on a one-electron picture, thus being orbital dependent and unsatisfactory from a physical point of view. We examine it under a truly invariant real space perspective, focusing on the role of electron delocalization. We show that this view, compatible with orbital thinking, overcomes its limitations. By examining simple model systems we show that it is electron delocalization that drives any singlet-triplet gap, and that delocalization and ionic mixing are two sides of the same reality. It is in the end delocalization, fostered or hindered by the specific structure of a system, that lies behind its preferred magnetic coupling mode. In the case of superexchange-mediated coupling through atomic bridges, we also point out the non-essential role of the bridge's electrons in setting up singlet-triplet preferences. We show that the use of real space thinking allows for tuning singlet-triplet gaps using knobs that are not easily grasped from the orbital standpoint, opening new avenues in the design and control of molecular magnets.

Introduction

The fascination of humankind by magnets has accompanied our species for millennia,¹ although it took a considerable amount of time and ingenuity until Faraday and Maxwell's systematizations led to the electromagnetic field equations. The discovery of the electron and its consecration at the International Congress of Physics held in Paris in 1900 laid the grounds to solve the problem of the sources of the fields, but opened others. Langevin, for instance, noted that paramagnetism required the existence of atoms with permanent magnetic moment, but it was not until Goudsmit and Uhlenbeck² demonstrated the existence of an intrinsic magnetic moment for the electron and Dirac combined Einstein's relativity with quantum mechanics,³ that the electron's spin was finally understood.

The rapid success of quantum theory in providing a successful explanation of magnetic phenomena was impressive, and by the early 1930's two influential books on the subject had already been written by Van Vleck (1932)⁴ and Stoner (1934).⁵ Since then, the theory of magnetic couplings has been intimately linked to the concept of exchange,⁶ and to various phenomenological models like those of Heisenberg, Dirac, and Van Vleck,^{4,6,7} or Ising.⁸ In the former, for instance, an effective spin Hamiltonian $H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$ is written in terms of intercenter magnetic exchange coupling constants J_{ij} , from which collective behaviors can be simulated and macroscopic susceptibilities computed. The J 's have been traditionally fitted against experimental results, and soon efforts were made to compute them *ab initio*. Historically (an authorized account can be found in the book by Mattis¹), this problem was initially tackled with the Heitler-London (HL) methodology, which coined much of the language still used today, but the inherent difficulties of using non-orthogonal one-electron functions in the incipient valence-bond (VB) theory led to catastrophic simplifications in dealing with any but the simplest systems. This led Slater,⁹ among others, to advocate for using orthogonal (Wannier) functions and ultimately to the adoption of the method of Mulliken and co-workers which resulted in molecular orbital (MO) theory.

In the simplest case of the bare coupling between two spin 1/2 centers, a and b , the

HL method predicts the correct singlet ground state when using just two localized non-orthogonal functions (φ_a, φ_b) , and has provided chemists with a set of primary tools with which to rationalize and control the magnetic interactions in a wealth of transition metal or organic radical compounds.¹⁰ In the weak overlap limit, the HL machinery leads to the Kahn-Briat (KB) model,¹¹ with a singlet-triplet splitting $\Delta_{ST} = E_S - E_T \approx 2K_{ab} + 4\beta S_{ab}$, where K_{ab} is the bare exchange integral between the a, b functions, β is the (negative) non-diagonal one-electron hamiltonian matrix element $\langle \varphi_a | h | \varphi_b \rangle$, and S_{ab} is the overlap integral $\langle \varphi_a | \varphi_b \rangle$. The use of localized orthogonal orbitals in the HL ansatz (the so-called Coulson-Fischer orbitals), gives rise to an unbound singlet, and to a triplet ground state, with $\Delta_{ST} = 2K_{ab}$. Slater himself⁹ showed that this catastrophic result can be remedied by mixing the covalent and ionic HL wavefunctions, introducing the idea that it is the larger variational flexibility of the singlet which stabilizes it below the triplet.

Meanwhile, the antiferromagnetic spin pattern revealed by neutron diffraction in MnO¹² led Anderson¹³ to explain the *inconceivably* large singlet coupling among the Mn²⁺ ions in terms of a modified version of Kramers'¹⁴ mediated spin-coupling theory. This superexchange mechanism is essentially a through-bond (instead of a through-space) coupling which is more efficient for singlets due to their larger variational space or, in more chemical terms, due to the presence of exchange pathways in the singlet that include ionic structures involving the bridging ligands, absent in the triplet. After several modifications, advanced by Goodenough, Kanamori, Anderson, and many others,^{15,16} Anderson's superexchange became the standard interpretive model of magnetic coupling through barriers for physicists.

In the chemical literature, the MO equivalent to the Kahn-Briat model appeared in 1975 in a seminal paper by Hay, Thibault, and Hoffmann¹⁷ (HTH). In its simplest version the pair of singly occupied orbitals obtained for the triplet state (those involved in the magnetic coupling), ϕ_1, ϕ_2 , are subjected to a localizing unitary rotation to give two orthogonal localized magnetic orbitals (OLOs), ϕ_a, ϕ_b . The variational space of this effective two-orbital, two-electron system contains two singlets and one triplet (being thus larger for the singlet).

Diagonalization in this 2×2 space followed by approximations equivalent to those of the Kahn-Briat model leads to $\Delta E_{ST} = 2K_{ab} - (\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab})$, where K_{ab} is the bare exchange integral between the OLOs, ϵ_1, ϵ_2 the orbital energies of the triplet state MOs, and J_{aa}, J_{ab} the onsite and inter-site Coulomb repulsions between the OLO's. A simple change of notation transforms the HTH expression into $\Delta E_{ST} = 2K_{ab} - 4t_{ab}^2/U$, where $t_{ab} = \langle \phi_a \bar{\phi}_b | H | \phi_a \bar{\phi}_a \rangle$ is the transfer integral and U Hubbard's on-site repulsion. It is not difficult to show with the help of quasi-degenerate perturbation theory¹⁸ that the presence of a closed-shell bridge (described by bridge localized orbitals) between the magnetic centers provides an equivalent ΔE_{ST} expression with an enhanced effective, or dressed, t_{ab}^{eff} element. This provides the MO basis for superexchange pathways.

Over the years, these ideas have crystallized in computationally efficient procedures that use large active spaces to capture the orbital quasi-degeneracies of the multi-electron states of transition metal ions, and in specific perturbation techniques, like the very successful difference dedicated configuration interaction method (DDCI) of Malrieu and co-workers,¹⁹ to deal with the multitude of exchange pathways and the subtleties of dynamic correlation. State of the art calculations are now precise to the cm^{-1} , representing accuracies of one part in 10^7 ,²⁰ and DFT methods, using broken symmetry approaches, have also been extremely successful.²¹ In most cases, calculations are interpreted by mapping back the results of the accurate computations onto HTH-like qualitative valence-only models that allegedly capture the essential physics of the problem.^{22,23}

The simplicity and ability of the HTH or KB models to rationalize the magnetic behavior of simple systems has forged several generations of chemists and physicists. The small, ever-present ferromagnetic direct exchange contributions are usually outweighed by generally *mediated* antiferromagnetic terms, which can be tuned by modulating the overlap integrals in the KB model or the transfer and on-site terms in the HTH expression. This has been also the basis for understanding magnetostructural correlations. For instance, the vast literature on dinuclear $3d$ complexes¹⁰ shows a subtle dependence of J with the bridging ligand (L)

and the $\widehat{\text{MLM}}$ angle (M is the metal). The rather rare ferromagnetic ground states are found near the allowed crossings of the ϵ_1 and ϵ_2 functions, i.e. when the KB overlap term $4\beta S_{ab}$ is zero or negligible and the positive K_{ab} prevails. When simple atoms act as bridging species, it is easily seen that such a crossing lies when the $\widehat{\text{MBM}}$ angle is close to 90° , in agreement with the experimental evidence.¹⁰

Despite the success of this simple orbital paradigm, its roots are conceptually unsatisfactory from several independent fronts, even when taking the dihydrogen molecule as the simplest possible model system. On one hand, if a non-orthogonal, HL, descriptions is used, the ground state is correctly assigned as a singlet at all internuclear separations. Partitioning J into ferromagnetic and antiferromagnetic contributions is here unjustified, for the K_{ab} integral is always smaller in magnitude than the other negative terms. On the other hand, if an orthogonal picture is assumed, the HL functions built with Coulson-Fischer orbitals leads to a catastrophic triplet unbound ground state. Finally, if a general orthogonal MO framework is adopted, a minimal configuration interaction mixing the two closed-shell singlet determinants is needed. Interpreting the results now requires an orbital localization step which provides the basic elements of the HTH machinery. Aside from cases where symmetry fixes the answer, the localization can be performed in infinitely many ways, and different values for the ferro- and antiferro- components of Δ_{ST} will be obtained thereafter.

In other words, since the prevailing magnetic spin coupling paradigm is based on a one-electron picture, it is orbital dependent. Any satisfactory explanation of the physics of magnetic coupling should be orbital invariant, a requisite that can be fulfilled by examining the problem in real space, as we advocate in the present work. As a simple example, it has been written many times that the HL unbound singlet built from Coulson-Fischer orbitals becomes stabilized in dihydrogen thanks to the mixing with ionic structures.²⁴ This is also, as already noted, the basis of the superexchange enhancement of J . However, the standard non-orthogonal HL singlet is a rather accurate approximation to the bound H_2 ground state, while VB-oriented contemporary researchers,²⁵ would surely agree that it does not contain

any ionic mixing. If a real space perspective is adopted, then it is clear that in all these cases a certain amount of ionic mixing exists, since when the tail of an a localized orbital approaches the b nucleus the probability of finding the two electrons in the b atom (an ionic contribution) is not zero.²⁶ Since the amount of ionic structures is easily found to be smaller (vide infra) in the Coulson-Fischer HL function, the argument of singlet stabilization by ionic mixing does actually work. In fact, as we are showing, there is no bonding and no singlet-triplet splitting without ionic mixing whatsoever.

It is our aim in this manuscript to offer a consistent real space story of magnetic spin coupling in the simplest possible model systems. As it will be seen, we have selected them to show our arguments with clarity, but our conclusions are of general validity. We will start by showing that electron delocalization is a necessary requisite for binding to occur, and that without it there can be no singlet-triplet splitting. When an orbital-free perspective is adopted, the K_{ab} ferromagnetic direct exchange gives way to antisymmetry based arguments that flow into the electron-electron repulsion energy components. We also show that angular dependent singlet-triplet switching occurs in the simplest H-He-H chain, even with minimal basis sets, when the overlap logic cannot simply work. This switching is present even when the atomic bridge is substituted by a one-electron pseudopotential, a finding that casts doubts on the true necessity of the superexchange mechanism. A real space perspective is then found to offer an orbital invariant view compatible with the basics of the HTH scheme, but independent of it. To that end, we apply a battery of real space techniques, using a quantum theory of atoms in molecules (QTAIM) atomic partition,²⁷ the interacting quantum atoms (IQA) energy decomposition,^{28,29} real space resonance structures from the theory of electron distribution functions (EDFs),^{30,31} and an open systems compatible local spin decomposition,³² among others. Altogether, these methods build a narrative in which antisymmetry requirements justify the success of orbital models, but overcome their limitations. We clearly show that singlets tend to be the electronic ground state in bridged systems when they are able to exploit their variational flexibility. This can be prevented, for

instance, and triplets can then become ground states, when the energetic cost of bending the bridge does not compensate configuration mixing. In this situation, the one-particle density of the singlet is forced to resemble considerably that of the triplet, much like in the case of the Coulson-Fischer HL function in H_2 . Being now the one-particle energy terms alike in both states, the larger mean interelectron separation of the triplet makes itself felt, and its smaller electron repulsion can make it fall below the singlet. We also find that the local energy of the two magnetic atoms evolves as the total energy of the system, supporting the non-essential energetic role of the bridge in determining the ground spin state. The systems are found to behave as rather localized diradicals, with relatively small local spins on the bridge. Although not essential, exchange pathways can also be sensed with our real space methodology, and we clearly show that they are more important in singlets, as expected.

We try to present our arguments as didactically as possible. First we provide a succinct summary of the model systems and model wavefunctions that we use, together with the real space techniques chosen. Then we show that strict localization leads to a necessarily unbound state in H_2 with no singlet-triplet gap. After this we study the H-He-H system and rationalize the singlet-triplet switching through an orbital-based energetic window that paves the way to the subsequent real space analysis.

Basic models and techniques

We consider the coupling of two $S = 1/2$ centers without and with an atomic bridge. The first case will be exemplified by the H_2 system, and the second by the H-He-H chain. Since we are considering four electrons at most, full configuration interaction (FCI) calculations provide appropriate solutions capturing the full physics of the problem. Minimal basis sets (STO-6G) as well as extended ones (6-311G(p)) will be used. All trends and qualitative results obtained with the extended bases are reproduced with the minimal sets, allowing an immediate fruitful chemical interpretation.

To perform real space analyses, a partition of space into chemically meaningful regions is in need. We choose the atomic partition provided by the quantum theory of atoms in molecules (QTAIM),²⁷ which provides a physically rooted decomposition. Only reduced density matrices (e.g. one- and two-particle densities) are used, so that the formalism is orbital invariant by construction. We also evaluate (see the SI for a succinct presentation) the probability of finding an exact, integer number of electrons in the different atomic regions, the so-called electron distribution functions (EDF),^{30,31} that provide the weights of real space resonance structures, the expectation values of the squared spin operator within an atomic region as well as that of the spin coupling between two regions,³² and perform an exact energy decomposition using the interacting quantum atoms methodology.^{28,29} In the latter, the total energy of a system is partitioned as a sum of local intra-atomic or self-energies, E_{self}^A , that take into account how much atoms deform when forming molecules, and pairwise additive interatomic interaction energies, E_{int}^{AB} , so that $E = \sum_A E_{self}^A + \sum_{A>B} E_{int}^{AB}$. The atomic self-energies are physically composed of the kinetic energy of their electrons, their attraction to the nucleus, and their mutual interelectron repulsion.

Let us label the magnetic centers as a and b . In the absence of bridge, the traditional non-orthogonal Heitler-London solutions for the singlet and triplet are

$$\psi_{S,T} = N_{\pm} (\varphi_a(1)\varphi_b(2) \pm \varphi_b(1)\varphi_a(2)) \times f_{S,T}, \quad (1)$$

where $f_{S,T} = (\alpha(1)\beta(2) \mp \beta(1)\alpha(2)) / \sqrt{2}$, φ_a, φ_b are $1s$ non-orthogonal functions centered at the a, b sites, and $N_{\pm} = 1 / \sqrt{2(1 \pm S_{ab}^2)}$. The covalent singlet HL ansatz provides a very reasonable description of H_2 binding, with $D_e \approx 96$ kcal/mol.³³ Mixing it with ionic structures leads to a covalent weight of about 0.76 and a much better $D_e = 105$ kcal/mol. The triplet is unbound, always above the singlet, and Δ_{ST} adopts the Kahn-Briat expression when S_{ab} is small enough. With a minimal STO-6G basis, $S_{ab} \approx 0.68$ at the equilibrium distance, so that the overlap tails are all but negligible. The spatial part of the wavefunction is symmet-

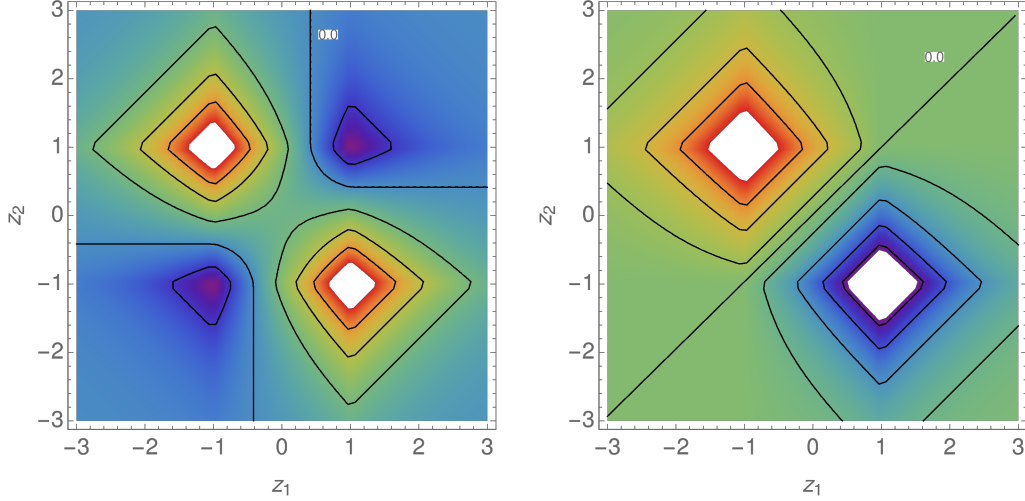


Figure 1: Projection density plot for $\psi_{S,T}^g(\mathbf{r}_1, \mathbf{r}_2)$ onto a plane containing the nuclei in the H_2 (left, right) molecule at an internuclear distance $R = 2$ au, as computed with $\varphi = \pi^{-1/2}e^{-r}$ 1s functions. The color code goes from dark blue to red, spanning the $[-0.15, +0.15]$ au range. The zero isoline has been highlighted, and white is used at saturation to avoid the nuclear cusps. The two electrons are constrained to move onto the internuclear z axis with nuclei at $(0.0, 0.0, \pm 1.0)$ au, the independent axes being the z_1 and z_2 coordinates.

ric/antisymmetric for the singlet/triplet, so that the singlet is nodeless, but the triplet is not. This increases the mean interelectron separation in the latter and leads to an electron density that, to first order in S_{ab} equals $\rho(\mathbf{r})_{S,T} = |\varphi_a(\mathbf{r})|^2 + |\varphi_b(\mathbf{r})|^2 \pm 2\varphi_a(\mathbf{r})\varphi_b(\mathbf{r})S_{ab}$.

Since modern electronic structure theory is MO based, the equivalent orthogonal picture starts with symmetry adapted functions $\phi_{g,u} = 1/\sqrt{2(1 \pm S_{ab})}(\varphi_a \pm \varphi_b)$. In this variational space there are two $^1\Sigma_g^+$ singlet determinants, $|\phi_g\bar{\phi}_g|$ and $|\phi_u\bar{\phi}_u|$, and one $^3\Sigma_u^+$ triplet, whose $M_S = 0$ component is $1\sqrt{2}(|\phi_g\bar{\phi}_u| - |\phi_u\bar{\phi}_g|)$. The variational space of the singlet is thus larger than that of the triplet. At the mean-field level, $|\phi_g\bar{\phi}_g|$ is the singlet ground state, with a 50% ionic component that can be decreased by CI mixing with $|\phi_u\bar{\phi}_u|$, leading to a solution indistinguishable from the covalent plus ionic HL resonance. It is very important to notice that the HL singlet built with φ_a and φ_b (ψ_S , Eq. 1) increases its $(\varphi_a(1)\varphi_a(2) + \varphi_b(1)\varphi_b(2))$ ionic component upon mixing, while the contrary is true when a CI(2,2) is performed on the Hartree-Fock (HF) determinant, i.e. mixing the $|\phi_g\bar{\phi}_g|$ and $|\phi_u\bar{\phi}_u|$ determinants. A full

consideration of these states in real space has already been presented.²⁶

Localized (Coulson-Fischer) orthogonal orbitals can be immediately built from the symmetry adapted gerade and ungerade functions: $\phi_{a,b} = 1/\sqrt{2}(\phi_g \pm \phi_u)$ (notice the use of ϕ instead of φ when using orthogonal functions). With these orbitals one can build HL-like singlet and triplet functions,

$$\psi_{S,T}^o = \frac{(\phi_a(1)\phi_b(2) \pm \phi_b(1)\phi_a(2))}{\sqrt{2}} \times f_{S,T} = \frac{(|\phi_a\bar{\phi}_b| \pm |\phi_b\bar{\phi}_a|)}{\sqrt{2}}. \quad (2)$$

When restated in terms of the canonical orbitals, these are simply the $1/\sqrt{2}(|\phi_g\bar{\phi}_g| - |\phi_u\bar{\phi}_u|)$ function for the singlet and the $1/\sqrt{2}(|\phi_g\bar{\phi}_u| - |\phi_u\bar{\phi}_g|)$ one for the triplet. Obviously, the triplet's space is one-dimensional and remains fixed in the canonical or localized pictures. The orthogonal HL singlet does not. Straightforward application of the Slater-Condon rules leads to $\Delta_{S,T}^o = 2K_{ab}$, where the exchange integral is computed over the localized orthogonal ϕ 's. The singlet is thus unbound and above the triplet, which is said to fall below the former as a consequence of Hund's rules in the case of two degenerate $\phi_{a,b}$ functions. Noticing that the two determinants differ in two spin-orbitals, the one-particle density matrices $\rho_1(\mathbf{r}_1; \mathbf{r}'_1)$ of the two states $\psi_{S,T}^o$ are equal, and so are the natural orbitals (with occupation equal to one in the singlet and the triplet), the electron densities, ρ , and the kinetic and electron-nucleus energies. Only the pair densities are different, with a $\Delta\rho_2(\mathbf{r}_1, \mathbf{r}_2)_{S,T} = 2\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_2)$ value that provides the $2K_{ab}$ energy difference. This is a crystal clear example of how a one-particle description (and thus the orbital model) *is insufficient* to understand even the simplest problems. Interestingly, given the orthogonality of ϕ_a and ϕ_b , the two orbitals are also orthogonal in any of the two equivalent atomic regions (for instance, in those provided by the QTAIM), so that $\int_a \phi_a(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r} = \int_b \phi_a(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r} = 0$. This implies (see the SI) that the localization and delocalization indices, that measure the degree of spatial electron delocalization,^{34,35} are identical in both states, i.e. that the ψ_S^o singlet is as (de)localized as the triplet ψ_T^o , and that the probability of finding two electrons (see also the SI) in any of

the atomic regions and none in the other, $p(2, 0)$, an orbital invariant descriptor of the ionic character of the wavefunction, is also equal in both states.²⁶ For instance, $p(2, 0) = 0.058$ when a 6-311G(p) basis set is used at $R = 1.42$ bohr. Let us recall that the HF singlet has $p(2, 0) = 0.25$ (and so the ionic terms weigh exactly 50%) and that the FCI one decreases this value to $p(2, 0) \approx 0.21$. This provides a clear clue about the weirdness of the ψ_S^o singlet. It displays the same density and the same number of electron pairs in each atomic basin, differing only in their average separation, which is higher in the triplet as a result of the antisymmetry of the same spin pair density, $\rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) = 0$. As it is clear from Fig. 1, the electrons try to stay away from each other in both states, but the two negative peaks along the main diagonal in the singlet give rise to a larger electron-electron repulsion. It is also interesting to understand how $p(2, 0)$, whose z projection is obtained after integrating the density displayed in Fig. 1 in the $(z_1 \geq 0, z_2 \geq 0)$ or the $(z_1 \leq 0, z_2 \leq 0)$ quadrants, can be equal in both states. The singlet displays a wider nodal line than the triplet, *violating both the nodeless nature of the ground state, and the Lieb-Mattis theorem*³⁶ for two electron systems. We stress that it is this artificially localized state which is used in one way or another to build magnetic coupling intuition in the orbital model. Both the bare K_{ab} values and the weights of the ionic mixing that transforms the ψ_S^o singlet into the ground state are as pathological as the ψ_S^o function itself. By preventing electron delocalization through the use of OLOs we artificially force the triplet below the singlet. And, as we show in the next section, not even in this case we avoid ionic mixing.

Electron delocalization and magnetic coupling

We now show that fully localized electrons prevent binding and any singlet-triplet splitting in our H_2 model. The proof is simple. Let us consider that each of the two electrons is spatially localized in one of the two equivalent atomic domains, and let us use the real space energetic stance provided by IQA (see the SI). The total energy of the system is

$E = E_{self}^a + E_{self}^b + E_{int}^{ab}$. Since the electrons are strictly localized, E_{self} can be built from the one-particle density matrix only, for no intra-domain electron-electron repulsion exists. It is thus the trace²⁸ of the H atom one-particle Hamiltonian over a density which is not variational, being thus above its *in vacuo* energy. Similarly, since one electron sits always in *a* while the other sits in *b*, the pair density is just the product of the densities for each electron, so that E_{int}^{ab} is the classical electrostatic interaction of two point nuclear charges and two symmetric extended electron densities. By Earnshaw's theorem,³⁷ this interaction energy is positive, so the final binding energy of the system is destabilizing at any internuclear distance: *localization prevents binding*.

We can now build an explicit solution for singlet and triplet states by imagining general ϕ_a and ϕ_b OLOs which are different from zero only in the *a* or *b* domains, respectively, i.e. $\phi_a(\mathbf{r}) = 0$ if $\mathbf{r} \in b$, and viceversa. The complex squares of these orbitals provide the electron density in each region. Properly symmetrized state functions for the singlet and triplet are immediately built as in Eq. 2. From them we can easily find that the one-particle density matrix is $\rho_1(\mathbf{r}; \mathbf{r}') = \phi_a(\mathbf{r})\phi_a^*(\mathbf{r}') + \phi_b(\mathbf{r})\phi_b^*(\mathbf{r}')$ and that the pair density becomes $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = |\phi_a(\mathbf{r}_1)|^2|\phi_b(\mathbf{r}_2)|^2 + |\phi_b(\mathbf{r}_1)|^2|\phi_a(\mathbf{r}_2)|^2$, regardless of whether the state is a singlet or a triplet, since $\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_2)$ is permanently zero for any \mathbf{r}_1 and \mathbf{r}_2 values. Since no difference exists now in the pair densities, $\Delta E_{S,T} = 0$. Thus, *a strict localization in real space prevents magnetic coupling*.

In our opinion, this academic example shows the potential problems of any orbital-based decomposition of $\Delta E_{S,T}$. The conducting wire filling the gaps is the amount of electron delocalization. If absent, no ionic structures are present, since the probability that the two electrons be found in the same region vanishes, $p(2, 0) = p(0, 2) = 0$, so $p(1, 1) = 1$, and no spin-triplet splitting arises. If present, both $p(2, 0)$ and $p(0, 2)$ are non-zero, and any OLOs-based description will also lead to positive K_{ab} and t_{ab}^2/U integrals which will conspire to offer the final orbital invariant J value. An eye-catching summary of these ideas can be found in Fig. 2. Separating artificially ferro and antiferromagnetic components depends on

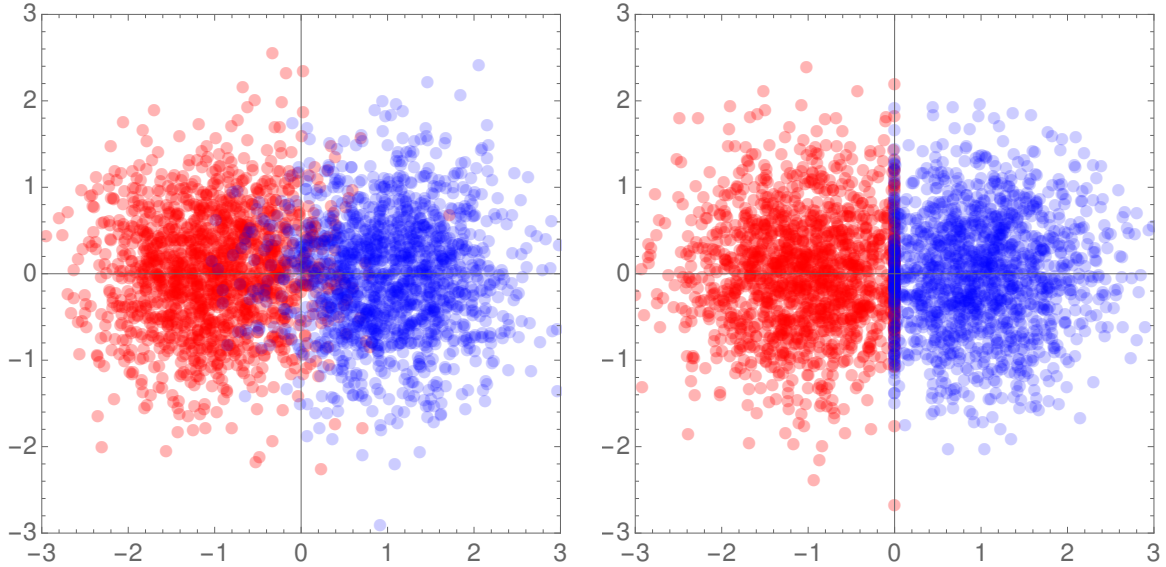


Figure 2: Statistical sampling of the positions of the two electrons of a model H_2 molecule with an internuclear distance of $R = 2$ bohr. In the left and right panels we allow and forbid, respectively, electron delocalization between the two equivalent atomic regions. The distribution has been projected onto a plane that contains the internuclear axis, with the nuclei at $0.0, 0.0, \pm 1.0$ bohr, so that the atomic division becomes the y axis. The two electrons are artificially labeled by color. Notice that when electrons delocalize, the probability that the two of them lie in, e.g., the left atom, as given by the $p(2,0)$ ionic probability described in the text, is non zero. In this case, binding as well as singlet-triplet splitting, occurs. On the contrary, when delocalization is forbidden, the *blue (red) electron remains always on the right (left) regions*. Any state like this is unbound and its singlet-triplet gap vanishes.

choosing a given orbital picture. As we have shown, allowing electrons to delocalize switches on both K_{ab} and ionic mixing, simultaneously. Considering them independent actors in the coupling game is not justified.

Coupling through an atomic bridge: the H-He-H orbital image

We now turn to consider the possibly simplest model system that displays a structural dependent switch of magnetic states: the symmetric H-He-H aggregate. Aside from van der Waals stabilized complexes, the ground state potential energy surface of this system collapses over a free He atom and a H_2 molecule, so we simply use constrained geometries to show our arguments. It is easily found that the system’s ground state is a singlet for linear configurations and a triplet when the H-He-H α angle is close to 90° . This order is maintained for a wide range of H-He R distances.

Being a four electron system, the H-He-H aggregate can be solved at the FCI level effortlessly with large basis sets. Although the quantitative energies and J splittings do obviously change with the quality of the basis set, interestingly the singlet-triplet state ordering is maintained even with minimal descriptions, so that clear qualitative chemical pictures can be drawn easily. Notice that in a minimal description no functions with $l > 0$ are used in the cases examined, so that both polarization effects as well as participation of higher energy virtual pathways have to be abandoned as key actors in the coupling. We have performed STO-6G (minimal) as well as 6-311G(p) (extended) FCI calculations at linear (L) and bent (B) geometries that exemplify the singlet-triplet switching. To understand the role of the atomic bridge, we have also added calculations for the isolated H_2 molecule at the same H-H separations. Since $\Delta E_{S,T}$ falls quickly with R , we report data for R values which provide splittings in the usual magnetic energy scale. We enforce D_{2h} and C_{2v} geometries for the L and B geometries, but it will suffice us to label states as a_1 or b_1 in C_{2v} symmetry. Our

main discussion will use $R_{\text{HeH}} = 1.2587 \text{ \AA}$, and α either 180° or 91.3° , with $R_{\text{HH}} = 1.8000 \text{ \AA}$ in the latter case. When analyzing triplets, we compute always the $M_S = 0$ component. To better understand the arguments below, Fig. 3 shows a sketch of the STO-6G orbital picture for both the singlet and the triplet states.

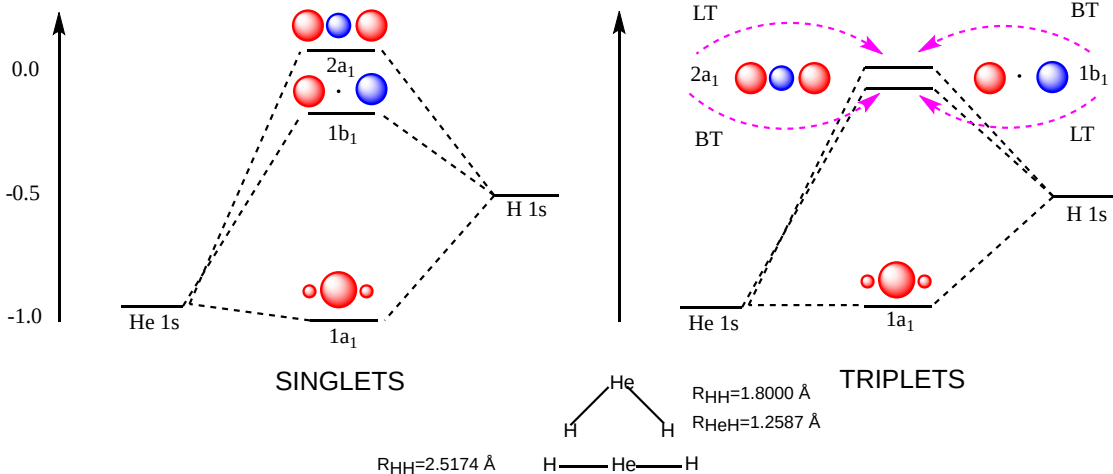


Figure 3: STO-6G orbital diagram for the minimum energy singlet and triplet states of H-He-H in both the linear and bent geometries. The canonical orbital energies ϵ have been drawn approximately on an energy scale in au. The magnetic orbitals of the two singlets and the two triplets show similar ϵ 's. Notice the ordering change in the $1b_1$ and $2a_1$ functions in the linear and bent triplet.

The extended calculations in H_2 yield academic results. At $R_{\text{HH}} = 2.5174 \text{ \AA}$, $\Delta E_{S,T} = -6.80 \text{ mE}_h$, and the wavefunction is dominated by two configurations, $\psi_S \approx 0.795|a_1\bar{a}_1| - 0.571|b_1\bar{b}_1| + \dots$, that lead to a_1 and b_1 natural orbitals with occupations equal to 1.302 and 0.698, respectively. At $R_{\text{HH}} = 1.8000 \text{ \AA}$, $\Delta E_{S,T} = -49.0 \text{ mE}_h$, and the wavefunction increases its single-determinant character, $\psi_S \approx 0.912|a_1\bar{a}_1| - 0.363|b_1\bar{b}_1| + \dots$, with natural orbital occupancies equal to 1.680 and 0.318, respectively. The triplets are in both cases almost pure, with $\psi_T \approx 0.707|a_1\bar{b}_1| - 0.707|b_1\bar{a}_1|$, as it is well known. Let us recall that both geometries are well past equilibrium, so that in the singlets the kinetic energy is lower than at dissociation, while the contrary is true for the triplets, which show smaller interelectron repulsion than that of their corresponding singlets thanks to their spatially antisymmetric wavefunctions. The singlets are in both cases rather far from the ψ_S^0 limit already discussed.

It is an interesting exercise to construct a pure ψ_S^o function from the triplet’s canonical orbitals (as done in conventional MO theory). At $R_{\text{HH}} = 2.5174 \text{ \AA}$, for instance, this HL Coulson-Fischer singlet lies 2.00 mE_h above the FCI triplet, a quantity which is essentially equal to the 2.07 mE_h increase in interelectron repulsion suffered by the triplet on going to the artificial Coulson-Fischer state.

Introduction of the He atomic bridge yields singlet linear and triplet bent ground states, and now $\Delta E_{S,T} = -21.2$ and $+4.2 \text{ mE}_h$ for the linear and bent configurations, respectively. The preferentially occupied canonical orbitals are a $1a_1$ function which is basically the 1s He orbital and two $2a_1$ and $1b_1$ functions in which the symmetric and antisymmetric combination of the 1s H orbitals dominate. We will call the latter the active a_1 and b_1 orbitals. The occupancy of the $1a_1$ natural orbital is greater than 1.98 in all cases, so that the orbital game basically involves the a_1 and b_1 functions, as expected.

Table 1: 6-311G(p) FCI data for the linear (L) and bent (B) H-He-H geometries described in the text. S stands for singlet and T for triplet, and ϕ is the same a_1 or b_1 function as that written explicitly in the determinant for the singlets, while it is the other one in the triplets. n are the occupation numbers of the $2a_1$ and $1b_1$ active natural orbitals. K, ne, ee are the total kinetic, nucleus-electron, and electron repulsion energies, and ϵ the canonical orbital energies. All data in au.

	LS	LT	BS	BT
E	-3.8328	-3.8116	-3.8102	-3.8144
K	3.9700	4.0902	4.1079	4.0788
ne	-12.3468	-12.4305	-12.6211	-12.5804
ee	2.6523	2.6369	2.7274	2.7116
$c(a_1\bar{\phi})$	-0.4983	0.7033	0.7360	0.7040
$c(b_1\bar{\phi})$	0.8601	-0.7033	-0.6288	-0.7040
$n(a_1)$	0.5044	0.9993	1.1700	0.9999
$n(b_1)$	1.4942	0.9992	0.8282	0.9997
$\epsilon(a_1)$	-0.0269	-0.0994	-0.0639	-0.1585
$\epsilon(b_1)$	-0.3124	-0.1854	-0.2854	-0.1286

Table 1 summarizes the extended FCI data. All wavefunctions are dominated by two configurations, and the triplets are very close to the open shell HF solution (or to the HL

function) due to their limited variational space. It is of utmost importance that the linear singlet (LS) preferentially occupied determinant is $|b_1\bar{b}_1|$, while the $|a_1\bar{a}_1|$ one dominates the bent one (BS), as in dihydrogen. Considering a mean-field (restricted open shell for the $M_S = 1$ triplet) solution helps in the discussion. The single-determinant LS, with configuration $1a_1^2 1b_1^2$ and $E_S = -3.6749$ au, is way above the LT, with configuration $1a_1^2 2a_1 1b_1$ and $E_T = -3.7746$ au. Moreover, a $1a_1^2 2a_1^2$ singlet built with the triplet's orbitals lies at $E = -3.4788$ au. The two nodal planes of the ϕ_{a_1} function give rise to a considerably higher kinetic energy, so that electrons prefer occupying the one-node ϕ_{b_1} function if forced on a single determinant. This gives rise to the linear triplet, with only one a_1 electron, falling below the singlet. The bridging atom thus acts as a Pauli barrier to the pumping of electrons into the H-H internuclear region, that now contains the He atom. In its absence, the H_2 subsystem prefers occupying the ϕ_{a_1} function. In its presence, this becomes a double node orbital, which is avoided. As shown in Table 1, configuration mixing renders a linear singlet ground state thanks to a sharp decrease in the kinetic energy.

Restriction to a minimal STO-6G basis, where no orbital polarization is allowed and the wavefunction structure is severely constrained, changes the quantitative, but not the qualitative picture. As expected, energy differences are decreased by the much lower orbital flexibility, but $\Delta E_{S,T} = -15.1$ and $+1.8$ mE_h in the L and B geometries.

Understanding the switch to a triplet ground state in the bent configuration starts by noticing that it clearly fulfills the expectations from the HTH model. Using the triplet's orbitals, the HTH $(\epsilon_{a_1} - \epsilon_{b_1})^2$ expression introduces a much larger antiferromagnetic term in the linear than in the bent configuration. Notice that no Kahn-Briat orthogonality arguments can be used here. From the physical perspective, it is interesting to acknowledge how close the energies of the BS, LT, and BT states are. This is particularly striking, since the bent H-H distance is considerably shorter than the linear one. Physically, it means that approaching the H atoms in the triplets does not vary the energy substantially, so that almost perfect nuclear shielding occurs that avoids the increased nuclear repulsions. Since symmetry constrains the

triplet functions (just notice the very close to 1.0 occupation numbers of the a_1, b_1 natural orbitals or their very close to $\pm 1/\sqrt{2}$ CI coefficients), an orbital localization leads to almost perfectly localized H functions. Contrarily, the LS is much more delocalized and, upon bending, it has to respond in order to shift electron density into the H-H region to shield the enlarged proton-proton repulsion. Since the b_1 function has a nodal plane forbidding this density accumulation, the response implies increasing the ϕ_{a_1} contribution, so that the coefficients of the $|a_1\bar{a}_1|$ and $|b_1\bar{b}_1|$ determinants approach those in the ψ_S^o model. With this, its kinetic energy and electron repulsion increase substantially upon bending (Table 1), but the ne attraction does its work to counteract the +0.084 au increase in the nn repulsion. In this process, the LS wavefunction approaches the ψ_S^o model, and the lower electron repulsion of the triplet does the trick.

Summarizing, the atomic bridge’s Pauli barrier drives the two electrons of the H_2 subsystem to prefer a b_1^2 configuration over a a_1^2 one in the LS. Configuration mixing leads to an inversion of the magnitude of the CI coefficients with respect to the free H_2 molecule, with an occupation number of the b_1 natural orbital larger than one and close to 1.5 (the b_1 occupation in the bare dihydrogen at the same internuclear separation is 0.698). On bending, the need to pump charge in between the hydrogens changes the bonding mode to a_1^2 , giving rise to a considerable electron reorganization that approaches the singlet to the weird Coulson-Fischer model. All triplets, on the contrary, are well localized at any geometry, suffering much smaller energy changes. It is thus possible to use orbital arguments to understand the singlet-triplet switching without invoking the HTH paradigm. Now we turn to show that a real space analysis provides a directly consistent narrative of the above ideas.

Coupling through an atomic bridge: the alternative real space picture

The analysis of wavefunctions in real space provides strong orbital invariant physical images. Local energies, electron localization and delocalization descriptors, the probabilities of different electron distributions, local spins, etc, are all available once an initial partition of the space into chemically appealing regions is available. As noted, we choose the QTAIM partition. A summary of the real space artillery can be found in the SI.

Table 2: 6-311G(p) FCI real space data for the H₂ molecule at the linear (L) and bent (B) H-He-H geometries. S stands for singlet and T for triplet. All data in au. The self-energy of the H atom *in vacuo* is -0.49981 au.

	LS	LT	BS	BT
ρ_{bcp}	0.0065	0.0049	0.0289	0.0116
$\nabla^2 \rho_{bcp}$	0.0103	0.0137	0.0176	0.0453
E_{self}^H	-0.4956	-0.4954	-0.4866	-0.4826
E_{int}	-0.0128	-0.0063	-0.0585	-0.0176
δ^{HH}	0.0920	0.0427	0.3503	0.1042
$p(2, 0)$	0.0230	0.0107	0.0876	0.0347
S_H^2	0.7155	0.7340	0.6186	0.6979

We start again by summarizing the bare H₂ results, which can be found in Table 2. At both geometries we are still in the closed-shell regime, where the Laplacian at the internuclear midpoint (the QTAIM bond critical point, bcp) is positive. As expected and known, the larger ϕ_{a1} occupation number of the singlet yields larger bonding densities, and less positive Laplacians. Also to be noticed are the larger deformation energies (defined as the self-energy cost of passing from an *in vacuo* atom to the *atom-in-the-molecule* situation, $E_{def}^A = E_{self} - E_{self}^{A,0}$) of the H atoms in the triplet as R_{HH} decreases, as well as the considerably larger electron delocalization indices found in the singlet. Yet, deformations are small in the regime examined, peaking at about 11 kcal/mol in the BT case. The amount of ionic structures, given by $p(2, 0) = p(0, 2)$, shows that even the triplet state leads to a measurable

delocalization and non-vanishing probability to find the two electrons in the same atomic region: the weight of ionic structures is approximately 5, 2, 17, and 7% for the LS, LT, BS, and BT states, respectively. The local spin analysis³² is compatible with the small overall delocalization. All systems are clear diradical species, coupled to singlet or triplet total spin states. The diradical character is larger in the triplet, also as expected.

Table 3: 6-311G(p) FCI real space data for the H-He-H system at the linear (L) and bent (B) geometries. S stands for singlet and T for triplet. The isolated FCI energies of the H and He atoms are -0.49981 and -2.89057 au, respectively. All data in au.

	LS	LT	BS	BT
ρ_{bcp}	0.0781	0.0685	0.0676	0.0705
$\nabla^2 \rho_{bcp}$	0.0917	0.1592	0.1750	0.1556
ρ_{bcp^*}	-	-	0.0268	0.0260
$\nabla^2 \rho_{bcp^*}$	-	-	0.1323	0.1373
Q^{He}	-0.0123	-0.0218	-0.0380	-0.0249
E_{self}^{He}	-2.7712	-2.7832	-2.7872	-2.7813
E_{self}^{H}	-0.4685	-0.4659	-0.4603	-0.4626
E_{self}^{HH}	-0.9423	-0.9306	-0.9839	-0.9881
E_{int}^{HeH}	-0.0597	-0.0489	-0.0468	-0.0504
E_{int}^{HH}	-0.0052	0.0012	-0.0082	-0.0062
δ^{HeH}	0.2442	0.2096	0.1967	0.2113
δ^{HH}	0.0824	0.0138	0.0750	0.0619
δ^3	0.0107	0.0061	0.0130	0.0146
$p(1, 2, 1)$	0.7278	0.7919	0.7792	0.7714
$p(0, 3, 1)$	0.0571	0.0529	0.0537	0.0537
$p(2, 1, 1)$	0.0528	0.0439	0.0364	0.0432
$p(2, 2, 0)$	0.0228	0.0051	0.0192	0.0161
S_{He}^2	0.198	0.181	0.154	0.183
S_{H}^2	0.663	0.712	0.690	0.717
$\mathbf{S}_{\text{He}} \cdot \mathbf{S}_{\text{H}}$	-0.050	-0.030	-0.039	-0.017
$\mathbf{S}_{\text{H}} \cdot \mathbf{S}_{\text{H}}$	-0.564	+0.209	-0.613	+0.200

Examining the inclusion of the He bridge in real space allows us to follow the change in all these properties smoothly. A summary of the data can be found in Table 3. Taking a look at just plain density descriptors, it is clearly found that all interactions are closed-shell like with positive Laplacians, and that the He-H bcps display density values which correlate with the observed ground state. This has been found to be general, *so that the interaction energy*

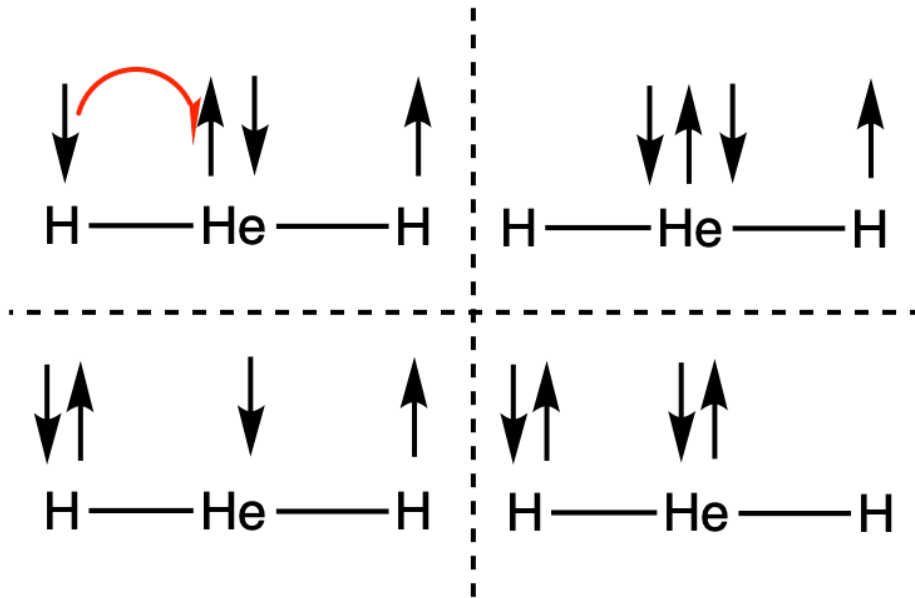


Figure 4: FCI/6311-G(p) dominant electron distributions of the several states of H-He-H, starting with the (1,2,1) one on the top-left panel. Both the top-right and bottom-left arrangements are H-He one-electron exchanges, but the bottom-right one, (2,2,0), implies either one direct H-H or two coupled H-He one-electron exchanges.

between the magnetic center and the bridge predicts the ground state. For the bent structures there is no H-H bcp, but we have also added density descriptors at the H-H midpoint (bcp* in the Table). Notice how the BS pumps density into the bcp* region, as expected from orbital arguments. Topological charges talk about a considerably electronegative He atom. This electronegativity is maximal when the interaction energy between the magnetic centers and the bridge (E_{int}^{HeH}) is small, as in the BS case, and decreases as the He-H interaction increases.

We turn now to the energetic realm. By comparing with the bare results of Table 2, it is found that the H atoms deformation is around 20 kcal/mol larger in the bridged systems. This is accompanied by sizable He deformation energies that reach 90 kcal/mol. The E_{self}^{He} values for the LT, BS, and BT systems are similar, in agreement with their overall energies, and the larger He deformation energy in LS points toward a more intense bonding. This is corroborated by comparing the E_{int}^{HeH} energies, which show a larger HeH interaction in this system. Notice that this descriptor does also correlate with the ground state, reinforcing

the previous paragraph. Notice also that the behaviour of E_{self}^{He} on going from the singlet to the triplet differs in the L and B geometries. This again reflects the different H-He bonding strengths.

An important insight is obtained from examining the energy of the H_2 subsystem in the triatomic. This is the E_{self}^{HH} quantity, which can be directly compared with the bare H_2 energy. The linear geometries distort more intensely the H_2 subsystem than the bent ones, as expected, but, most importantly, the energetic ordering of the subsystem is again correlated with the total ground state. This means that if the electronic structure of the dihydrogen subsystem is appropriately modified by the bridge but the latter is afterwards ignored, the sign of J is appropriately predicted. This casts doubts on the necessity of the bridge to understand magnetic couplings, see below. Quantitatively speaking, at the linear configuration $\Delta E_{S,T}$ for the H_2 subsystem is enhanced from -6.8 to -11.7 mE_h on introducing the bridge, a value to be compared to the total H-He-H $\Delta E_{S,T}$ of -22.6 mE_h . This shows that the presence of the He atom is not necessary to yield the correct ground state, but that it clearly contributes to the singlet-triplet gap, as expected from all the accumulated MO knowledge. Similarly, at the bent geometry, we pass from -49.0 to +4.2 to +2.8 mE_h , respectively, and the He atom contributes stabilizing slightly the singlet with respect to the triplet as a result of the smaller He deformation in the singlet.

Regarding electron delocalization, electrons prefer to delocalize with the He bridge, as evidenced by the much larger δ^{HeH} than δ^{HH} values in all cases. The former does also correlate with the preferred ground state, so that increased He-H interaction leads to smaller energy. We stress that the smaller E_{int}^{HeH} in the BS with respect to the BT indicates that the electronic structure reorganization that is needed for the BS to minimize its energy and shield the increased nn repulsions upon bending hinders direct HeH delocalization, in complete agreement with the previous orbital analysis. The HH delocalization index behavior is also illuminating. In the linear geometries it is much larger in the singlet, which displays a value similar to that found in the bare dihydrogen molecule. Contrarily, the BS and

BT show similar δ^{HH} values, which contrast with the bare H_2 data of Table 2. The three-center delocalization index, measuring simultaneous three-body population fluctuations,³⁸ is positive and small, correlating again with the ground state preference.

Let us jump to consider the role of ionic structures. A reasonable route to identify exchange pathways in real space is the consideration of the probability of finding different electron arrangements, as found in the fourth set of rows in Table 3 and in Fig. 4. We consider the atoms in the H,He,H order, so that $p(1, 2, 1)$ refers to the probability of finding one electron in each H atom and two in Helium. The neutral structure with one electron in each H atom and two in the He bridge dominates, being a minimum in the LS, and a maximum in the LT. As expected from the HTH rationale, the one-electron exchanges from H to He, as given by $p(0, 3, 1)$ and $p(2, 1, 1)$, are maximum in the LS, which corroborates the enhancing role of the bridge in stabilizing the singlet in the linear geometry. The sum of both probabilities correlates with the He-H interaction, and tells the traditional story about how exchange with the bridge's electrons is facilitated in singlets but not in triplets. A relevant point here is that it is $p(2, 1, 1)$ which is considerably hindered in the BS, not $p(0, 3, 1)$. This has a very simple rationalization in terms of our basic shielding argument. Too many electrons in the H regions do not help in this case (they increase the electron repulsion between the two Hs). Finally, $p(2, 2, 0)$ is a measure of direct H-H delocalization. Comparing it with $p(2, 0)$ in the bare H_2 molecule gives rise to the same narrative already commented when explaining the δ^{HH} values. It is maximum and minimum for the LS and LT systems, and the two bent systems provide similar small values.

We leave the local spin analysis³² for the end of this section. A pictorial representation is found in Fig. 5. It is first noteworthy to notice that the He atom holds a residual, though non-negligible squared spin. This is a result of H-He delocalization and, in consequence, largest for LS, and smallest for BS. This spin transfer leads to a partial quenching of the spin at the magnetic centers. It would be interesting to examine to what point this affects the hypothesis leading to Heisenberg modeling in real magnetic systems. Secondly, the local spins of the H

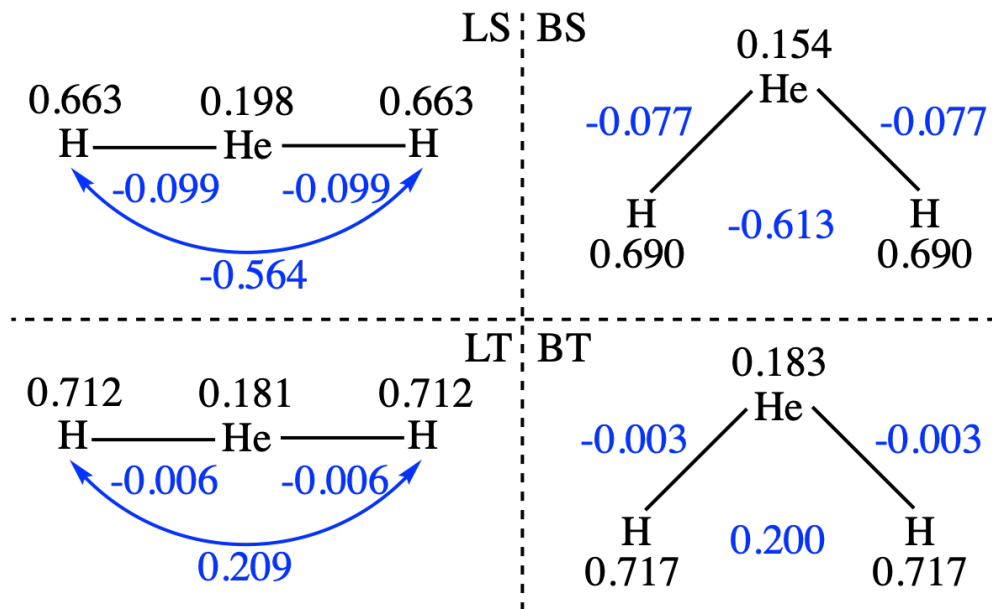


Figure 5: FCI/6311-G(p) local spin analysis for the H-He-H system. $\langle S_A^2 \rangle$ values in black, $\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle$ couplings in blue.

atoms are rather large in all cases, approaching the strictly localized values of $3/4 = 0.75$. In this sense, all the systems behave as rather localized diradical species. The worst localized LS system shows the largest deviations of this limiting model. As the atomic spin couplings are regarded, recall that negative/positive $\mathbf{S}_i \cdot \mathbf{S}_j$ imply anti/ferromagnetic behaviour. The H-He values are all small, particularly in the triplets, favoring the local magnetic image, and negative. This is important, since in the triplets each He,H pair couples very weakly and antiferromagnetically, as it would be expected from standard weak chemical bonding.³² It also means that all ferromagnetic coupling in the triplets lies between the H atoms, again supporting a localized picture. Finally, we comment on the $\mathbf{S}_H \cdot \mathbf{S}_H$ values. Admitting the Heisenberg picture, with $H = -J_{HH}\mathbf{S}_H \cdot \mathbf{S}_H$, $\Delta E_{S,T}$ would arise from $-0.773J$ in the linear and from $-0.813J$ in the bent configurations. This is also worthwhile exploring in the future.

Are the bridge’s electrons needed at all?

The real space picture we have just detailed provides a physical explanation of the magnetic coupling phenomenology that is dealt with, for instance, the HTH model. Moreover, real space reasonings lack the problems associated to orbital arbitrariness, although they are many times criticized for their lack of predictivity. We now show that they can lead to truly new insights.

As it has been shown, the basic role of the atomic bridge is to impose a Pauli barrier to the presence of electrons, leading to a b_1^2 instead of a_1^2 preferred configuration in linear geometries. Chemical interaction with the barrier enhances the J values, but is not essential in the singlet-triplet preference, i.e. in determining the sign of J . It is thus strongly suggested by our findings that any object that is able to divert electrons from invading it, will elicit the observed behavior when it is put in between the two magnetic centers. This hypothesis is easily verified if we use a pseudopotential or effective core potential (ECP) to simulate the bridge. In our case it leads to a two-electron system, so that to circumvent the Lieb-Mattis theorem,³⁶ we must choose a non-local potential, for instance one that includes non-local projection operators of the $|\phi\rangle\langle\phi|$ form. We have chosen a standard He core ECP with p and $s - p$ components (see the SI for details) to simulate our systems again. Both at the 6-311G(p) and STO-6G FCI levels we reproduce the singlet to triplet ground state switching as we bend the system. We have found this to be also the case in other systems examined, like in the Li-Be-Li moiety. Table 4 summarizes the results. Notice that the ECP is absorbed as a one-electron contribution. $\Delta E_{S,T} = -24.1$ and $+4.3$ mE_h for the L and B geometries, quite consistent with the global FCI values already presented.

As shown, the substitution of the He moiety by an effective non-local potential does not alter the picture much, as expected from the overall good performance of ECPs in modeling the electron structure of molecules. Grossly speaking, much as the main job of standard ECPs is to avoid the variational collapse of valence electrons over the cores by maintaining the nodal structure of the former, here the He ECP avoids invasion of the He

Table 4: 6-311G(p) FCI data for the linear (L) and bent (B) H-V-H geometries described in the text in the presence of an ECP modeling the He atom, represented as V. S stands for singlet and T for triplet, and ϕ is the same a_1 or b_1 function as that written explicitly in the determinant for the singlets, while it is the other one in the triplets. n is the occupation number of the $2a_1$ and $1b_1$ active natural orbitals. K, ne, ee are the total kinetic, nucleus-electron, and electron repulsion energies, and ϵ the canonical orbital energies. ECP is the one-electron expectation value of the effective core potential. All data in au.

	LS	LT	BS	BT
E	-0.8928	-0.8687	-0.8669	-0.8712
K	1.1799	1.2416	1.2499	1.2360
ne	-2.5467	-2.6226	-2.7784	-2.7614
ee	0.2178	0.2026	0.2734	0.2691
ECP	0.0461	0.0995	0.0945	0.0910
$c(a_1\bar{\phi})$	-0.5236	0.7071	0.7094	0.7070
$c(b_1\bar{\phi})$	0.8517	-0.7071	-0.6467	-0.7070
$n(a_1)$	0.5483	0.9999	1.0327	0.9997
$n(b_1)$	1.4509	0.9999	0.9669	0.9997
$\epsilon(a_1)$	-0.1654	-0.3925	-0.2499	-0.4609
$\epsilon(b_1)$	-0.0078	-0.4826	-0.0022	-0.4336
ρ_{bcp*}	-	-	0.0141	0.0147
$\nabla^2 \rho_{bcp*}$	-	-	0.0536	0.0577
E_{self}^H	-0.4630	-0.4826	-0.4752	-0.4746
E_{int}^{HH}	-0.0129	-0.0031	-0.0108	-0.0131
δ^{HH}	0.1455	0.0277	0.0722	0.0837
$p(2, 0)$	0.0364	0.0070	0.0181	0.0209
S_H^2	0.6954	0.7395	0.7228	0.7187

nuclear region, reinforcing our points above. Since most of the descriptors in Table 4 follow the same trends as those already discussed in Tables 1-3, we will only comment on a few of them. On the one hand, the majority of ECP orbital descriptors evolve as in the full electron calculation, particularly the kinetic and electron repulsion energies, as well as the a_1 and b_1 natural occupations. The large b_1^2 contribution in the LS lies again behind its large δ^{HH} value. Similarly, as in the full electron calculation, the LT system displays the lowest ionic contribution. On the other hand, the total FCI energies excluding the ECP one-electron potential contributions favor the triplet in both the linear and angular configuration. The ECP row of Table 4 shows that the destabilizing effect of the pseudopotential is about 0.05 au lower in the LS than in any of the LT, BS, or BT geometries, in line with the stabilizing singlet contributions of the HTH model.

Finally, it is noteworthy that in the absence of the perturbing effect of the He electrons, the traditional correlation between stability and density at the critical point is also found in the bent configuration. The more stable triplet leads to the largest ρ_{bcp^*} . This has been found quite general in several cases, see below.

Tuning the coupling in real space

Using the insights derived above regarding the physical role of the bridge, it is illuminating to examine how the singlet-triplet gaps evolve when the nature of the bridge is modified. This can be done without leaving the toy models we have explored so far. We briefly review the outcome of: a) substituting the He closed-shell barrier by an absorbing He^{2+} potential; b) allowing for the electrons of the barrier to significantly mix with the magnetic states by changing He by a Be^{2+} core c) using a more realistic Li-Be-Li triatomic system to show how the results resemble those of the the H-He-H example. The full data can be found in the supplementary information.

Removing the He core while maintaining the linear and bent geometries already examined

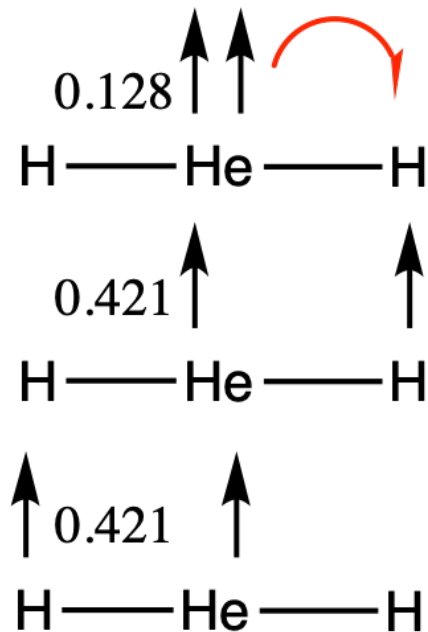


Figure 6: FCI/6311-G(p) dominant probability distribution of the LT state of H-He-H²⁺ at $R_{\text{HHe}} = 1.2587 \text{ \AA}$.

provides a very deep attractive potential to the electrons residing in the magnetic centers, since the orbital energy of the He 1s orbital is about -0.917 au . This means that a huge electronegativity difference exists that forces the electrons to invade the He region. Since the orbital energy of the $2a_1$ function is more negative than that of the $1b_1$ one in the LT and BT states, both prefer a predominant $1a_1 2a_1$ configuration that maximizes the now allowed delocalization. As the LS and BS states are regarded, they can be considered distorted He atoms, with very small H atomic basins (hosting about $6 \text{ } e$). Their FCI wavefunctions are fully dominated by the HF $1a_1^2$ configuration, with coefficients larger than 0.995. In the linear configuration, $\Delta E_{S,T} = -402.5 \text{ kcal/mol}$ at the FCI/6-311(p) level. Bending does not alter the picture and the gap is now -369.7 kcal/mol . However, since $\Delta E_{S,T} = -689.6 \text{ kcal/mol}$ for the He atom at the current FCI level, a considerable lowering of the triplet energy is obtained by delocalizing into the H basins, which now host $0.451 \text{ } e$ each in the LT configuration. Its probability distribution of finding electrons in the H, He, H basins, respectively is dominated by three contributions: $p(1, 1, 0) = p(0, 1, 1) = 0.421$ and $p(0, 2, 0) = 0.128$, with a considerable H-He delocalization index of 0.148, and a remarkable

H-H one rising to 0.354, see Fig. 6. This shows how the pure He triplet is avoided. A local spin analysis (SI) shows that the spin coupling between the two H regions is essentially negligible (even slightly antiferromagnetic, $\langle \mathbf{S}_H \cdot \mathbf{S}_H \rangle \approx -0.0009$). This example offers a global picture of atomic-like singlets and delocalized triplets, very far from the isolated magnetic centers already discussed. In real space, removing the Pauli barrier fosters delocalization, and this is much more efficient in the singlets, irrespective of the geometry.

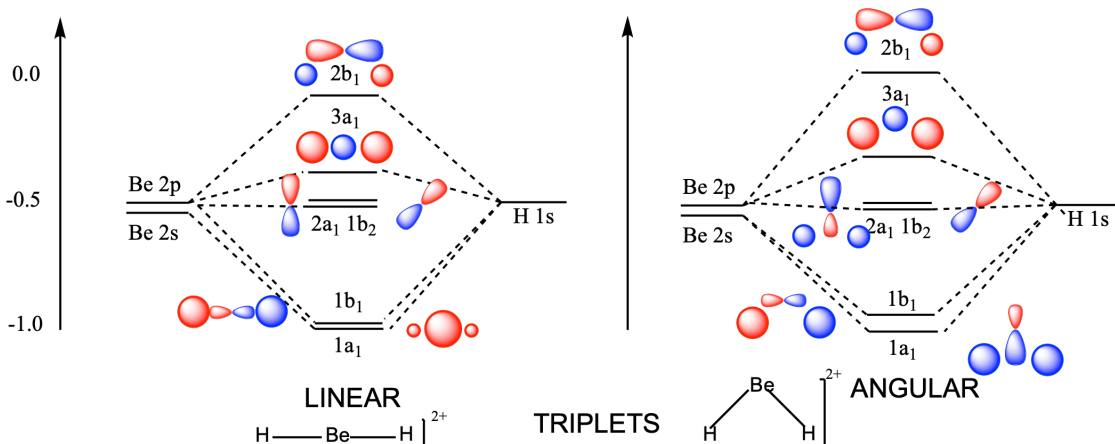


Figure 7: STO-6G orbital diagram for the linear and bent triplet states of H-Be-H²⁺ in both the linear and bent geometries. The canonical orbital energies have been drawn approximately on an energy scale in au, and the Be 1s core has been excluded.

The scenario changes completely if the Pauli barrier is substituted by available states that can mix strongly with the magnetic centers. This is easily done by introducing a Be²⁺ bridge, with $\epsilon_{2s,2p} \approx -0.665, -0.519$ au, respectively, when a 6-311G(p) basis is used. At the fixed linear and bent geometries examined, the FCI $\Delta_{S,T}$ are +243 and -11724 cm⁻¹, respectively, so now the triplet is the ground state in the linear geometry. As in our main example, this ordering is stable even at the STO-6G level. Fig. 7 shows the qualitative orbital diagram for the two triplet states. The BS falls well below the BT thanks to the polarizable nature of the Be states (the presence of available 2p functions in orbital parlance). The dominant $1a_1^2$ coefficient in the BS CI expansion is 0.922, showing that the H-He-H constraints forcing the BS to resemble the Coulson-Fischer singlet have now disappeared. Interestingly, it is now the orbital energies of the $1a_1, 1b_1$ states in the LS that are extremely

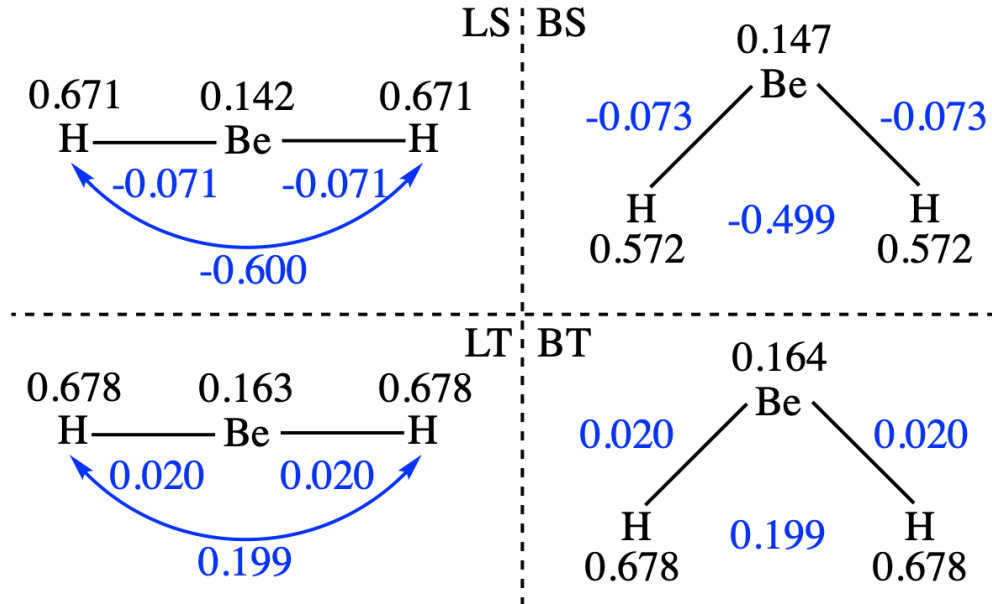


Figure 8: FCI/6311-G(p) local spin analysis for the H-Be-H²⁺ system. $\langle S_A^2 \rangle$ values in black, $\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle$ couplings in blue.

close, $-0.981, -0.974$ au, respectively. This allows the HTH expression to predict a possible triplet ground state. Now the physical root of this behavior is the considerably larger kinetic energy of the ϕ_{1a_1} with respect to ϕ_{1b_1} , at variance with the He barrier. Although the b_1 function has a nodal plane, its He contribution is 2p-like, with a considerably smaller kinetic energy than the 2s one. This effect is now the driving force that gives rise to a strong singlet mixing, $\Psi_{BS} \approx 0.722|1a_1 1\bar{a}_1| - 0.690|1b_1 1\bar{b}_1|$, switching on the Coulson-Fischer behavior of the singlet. All real space descriptors show that the triplet should be preferred. For instance, $\delta^{HH} = 0.0177, 0.0180$ and $\delta^{HHe} = 0.186, 0.188$ for the LS and LT states, respectively. Almost all of the linear singlet-triplet gap of 0.69 kcal/mol (1.1 mE_h) can be ascribed to a change in the self-energy of the Be atom, which passes from -13.7574 to -13.7588 au on going from the LS to the LT. The local spin analysis (Fig. 8) shows very clearly that the localized magnetic centers picture applies rather well in the LS (singlet diradical), LT, and BT cases, and that clear signs of H-H bonding appear in the BS case, since the H atom local spin is now considerably quenched, and the H-H singlet coupling decreased, with respect to the LS state. This is corroborated by examining the delocalization indices and the distribution

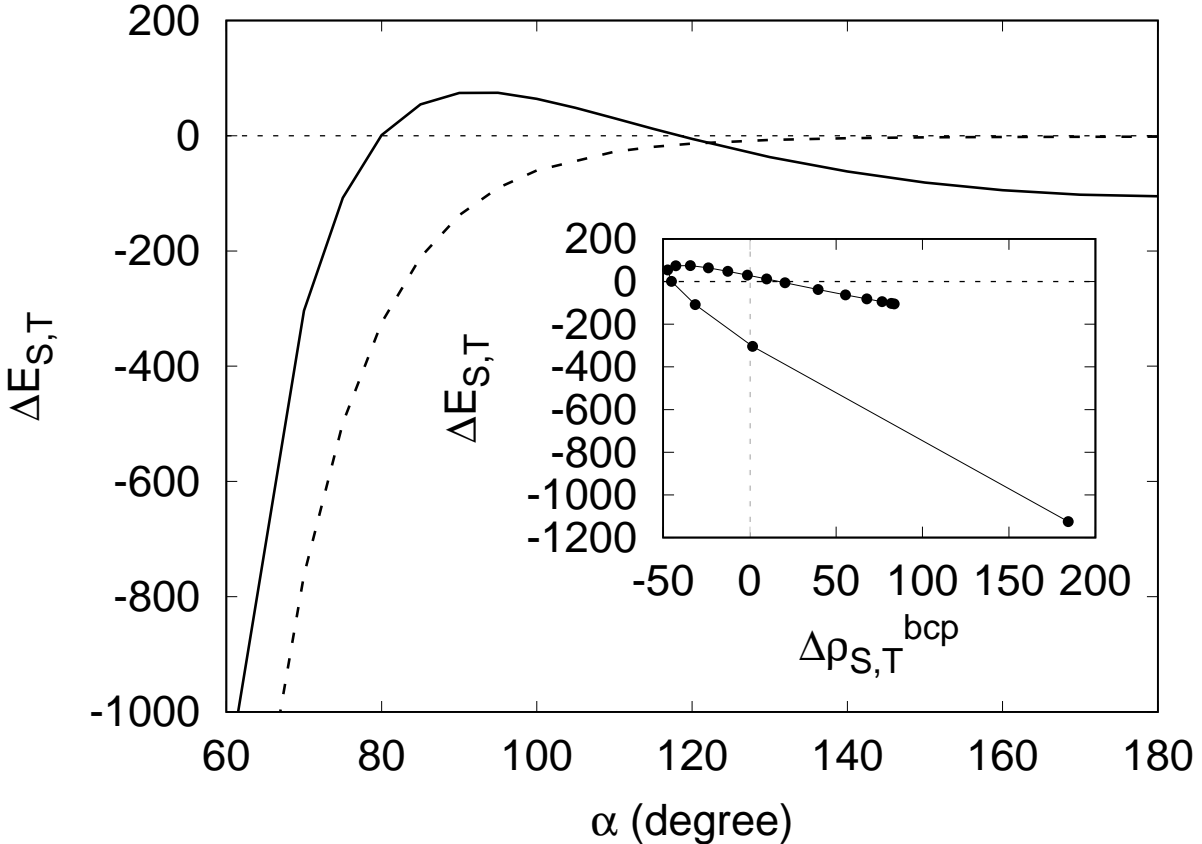


Figure 9: Singlet–Triplet splitting in Li_2Be (dashed line). The bare Li_2 behavior is also included for comparison (solid line). The inset shows the $\Delta E_{S,T} - \Delta \rho_{S,T}^{bcp}$ correlation in the weak coupling regime (upper branch) and in the Li_2 molecule regime (lower branch). Energies in cm^{-1} and densities in μe .

function probabilities. A polarizable (in contrast to a rigid) atomic bridge with shallow available states provides a triplet linear ground state with interesting real space branches.

To show that our real space arguments can be applied to similar cases, we show the weak interacting behavior of the Li-Be-Li system at $R_{\text{LiBe}} = 8.00$ au as we change the $\alpha = \widehat{\text{LiBeLi}}$ angle. In the weak-coupling region a CAS[4,7]//6-311+G** wavefunction is of sufficient quality. We only consider how the change in the density at the Li-Be bond critical point evolves with the singlet-triplet gap, shown in Fig. 9. Notice that we can again classify the Be bridge as a Pauli barrier, so that we expect the same behavior as in H-He-H. The bridge clearly amplifies the gap, and provides a triplet ground state at intermediate angles. $\Delta \rho$ at the Li–Be bcp’s is a good predictor of $\Delta E_{S,T}$: the state that accumulates more electron

density in the Li–Be bonding region is the most stable. The $\Delta E_{S,T}$ versus $\Delta\rho_{bcp}$ curve has two branches: one corresponding to the low angle regime, and another one to the high angle one. The spatial antisymmetry of the triplet is again important to explain the angular dependence of its energy. This state must show a slight density depletion at the Li–Li midpoint, which necessarily means a charge buildup out of the Li–Li axis. For α angles smaller than about 120 degrees, such accumulation lies well into the Li–Be bonding region, and the triplet falls below the singlet. At smaller angles the Li–Li distance decreases, and an incipient Li–Li bond forms so that density starts to accumulate again in between the lithiums, and the Li–Li bcp takes over the Li–Be bond, which ceases to determine the behavior of the system (the lower branch of the inset). In this region, the singlet’s energy falls quickly, approaching the curve of the bare Li_2 .

Conclusions

Physically understanding the roots of the coupling between magnetic centers in the simplest molecular systems is of utmost importance. This knowledge is used to build the models with which we describe the collective magnetic behavior of more complex entities, that ultimately leads to the design and synthesis of novel functional magnetic materials. The problem has been attacked since the earliest days of quantum mechanics and, after the development of modern computational techniques, it is now possible to predict, sometimes even quantitatively, magnetic coupling constants in complex materials *ab initio*. When the simplest two magnetic centers case is examined, molecular orbital theory led to the Hay, Thilbeault, and Hoffmann (HTH) model, which relies in the use of orthogonal localized magnetic orbitals. The HTH model has become the qualitative paradigm used to interpret the origins of singlet-triplet gaps, characterized by a direct ferromagnetic contribution given by the exchange integral K_{ab} between the magnetic orbitals, and a counteracting antiferromagnetic term rooted in the larger variational flexibility of the singlet state, that implies a magnetic

exchange mediated by ionic contributions. It also provides the basic ingredients to rationalize the singlet-triplet preference (an example of the so-called magnetostructural correlations) in simple dinuclear metallic complexes.

Successful as it has been, the HTH (or its equivalent Kahn-Briat variant) paradigm rests on a given choice of orthogonal one-electron functions out of an infinitely many set of possibilities. For instance, both the direct exchange as well as the ionic antiferromagnetic contributions can be manipulated, almost at will, by performing unitary rotations of the orbital space. It is then very relevant to examine the problem from an orbital invariant perspective, as that offered by real space analyses. We have concentrated on the very simplest two-center cases that can be imagined, the dihydrogen molecule and the H-He-H system, which already shows a singlet to triplet switch as we bend the H-He-H angle.

We have first shown that it is electron delocalization that drives any singlet-triplet gap and any ionic mixing. It is shown that delocalization and ionic mixing are two sides of the same coin, so that if the HTH paradigm can be restated in an orbital invariant framework, electron delocalization measures should play a major role. By examining the behavior of the H-He-H system using both orbital arguments and then real space ones, we demonstrate that it is the Pauli barrier introduced by the atomic bridge that crafts the electronic structure of the system. It does so by driving the system to choose the antisymmetric linear combination of the H orbitals instead of the normal symmetric one, in an effort to decrease the electron's kinetic energy. In the linear structure, configuration mixing allows the system to come to a beneficial compromise. Bending leads to a new energetic balance that can only be achieved by letting the singlet electron density resemble that of the triplet. In doing this, its advantage is lost.

Second, we have demonstrated that delocalization, allowed or prevented by the different symmetry of the wavefunctions of singlets and triplets, lies behind the preferred coupling mode. In this sense, a real space picture provides direct access to this concept. The systems behave as diradial species, although a non-negligible amount of spin is transferred to the

bridging atom. As noticed, local spin analyses might have an impact on how state-of-the-art calculations can be used to obtain J coupling constants, and deserve further consideration. Similarly, local energy techniques demonstrate that although the bridge amplifies the stabilization of the singlet in the linear geometry, as it is well known from the HTH model, all the qualitative features including the singlet-triplet preference lie within the subsystem formed by the two magnetic atoms. The amplification of the singlet stabilization induced by the bridge can be measured by the metal-bridge interaction energy, which makes full chemical sense. A number of bridge-magnetic center (He-H) real space interaction descriptors (bond critical point densities, interaction energies, etc) correlate with the singlet-triplet gap. We have also shown that exchange pathways can be clearly sensed by studying the probabilities of different electron distributions, all of them orbital invariant.

Finally, our findings have pointed toward the non-essential role of the atomic bridge's electrons in setting up the magnetic coupling. To check this idea, we have substituted the bridge by an effective core potential. Not unexpectedly, the absence of the bridge's electrons does not alter the singlet-triplet ordering, showing that any object that mimics appropriately the Pauli barrier of the bridge will induce the correct sign of the singlet-triplet gap. As shown, the nature of the wavefunctions of the singlet and triplet states, as analyzed in real space, follows closely the all-electron results.

Tuning the singlet-triplet gap is also possible using real space thinking. We have shown how this is modified examining three simple cases where the bridge is transformed into an electron absorbing center at two different energies and when a more realistic system, Li-Be-Li is examined.

Real space analyses thus question the accepted magnetic coupling paradigm based on orbital thinking from several different angles. We believe that new avenues can be opened by using these orbital invariant techniques to understand magnetic behavior that may be not obvious from other perspectives.

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Questioning the orbital picture of magnetic spin coupling:
a real space alternative

Electronic Supplementary Information.

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July 27, 2021

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1 Real Space Chemical bonding in a nutshell

Real space reasoning uses proper quantum mechanical observables to construct orbital invariant descriptors with chemical meaning. Among them, all reduced densities and density matrices (RDs, RDMs). An identification of spatial regions with chemical concepts is also necessary. This is usually done through spatial partitionings, normally induced by the topology of a scalar field. For instance, the topology of the electron density, ρ , induces an atomic partitioning: the Quantum Theory of Atoms in Molecules (QTAIM) explored by R. F. W. Bader and coworkers.¹ Similarly, the topology of Becke and Edgecombe’s² electron localization function (ELF) provides a partition into cores, lone pairs and bonding domains, etc.

Once atoms (or electron-pair domains) are available, chemical bonding descriptors are built. Both the electron-counting perspective (leading to populations and bond orders) as well as the energetic view that provides bond strengths are needed. These are offered by, for instance, electron distribution functions (EDFs) and the interacting quantum atoms approach (IQA).

1.1 The energetic face of bonding: Interacting Quantum Atoms

Given an atomic spatial partitioning, the interacting quantum atoms (IQA) energy partition considers the one- and two-domain division of the non-relativistic Born-Oppenheimer electronic energy³ described in the following equation,

$$\begin{aligned} E &= \sum_A E_{\text{self}}^A + \sum_{A>B} E_{\text{int}}^{\text{AB}} \\ &= \sum_A T^A + V_{\text{ne}}^{\text{AA}} + V_{\text{ee}}^{\text{AA}} + \sum_{A>B} V_{\text{nn}}^{\text{AB}} + V_{\text{ne}}^{\text{AB}} + V_{\text{ne}}^{\text{BA}} + V_{\text{ee}}^{\text{AB}}, \end{aligned} \quad (1)$$

wherein E_{self}^A and $E_{\text{int}}^{\text{AB}}$ are the IQA self and interaction energies of atom A and pair AB, while T^A denotes the kinetic energy of atom A. Finally, the terms $V_{\text{ne}}^{\text{AB}}$ and $V_{\text{ee}}^{\text{AB}}$ stand for (i) the attraction between the nucleus of domain A and the electrons of atom B and (ii) the repulsion between the electrons in atom A with those in basin B, respectively. The self-energy of an atom is the trace of its *in vacuo* Hamiltonian over the atomic region it occupies in a molecule. In a process where the atoms of a system dissociate their self-energies tend to the free atomic energies.

We can get further insight about the nature of the interaction between two atoms by separating the electronic repulsion into its Coulombic and exchange-correlation components. This splitting allows, in turn, the separation of the IQA interaction energy of a pair AB as³

$$E_{\text{int}}^{\text{AB}} = V_{\text{cl}}^{\text{AB}} + V_{\text{xc}}^{\text{AB}} = E_{\text{ion}}^{\text{AB}} + E_{\text{cov}}^{\text{AB}}. \quad (2)$$

Usually binding is measured relative to appropriate reference for the quantum fragments A , with $E^{A,0}$ energies. Then $E_{\text{self}}^A - E^{A,0} = E_{\text{def}}^A$ is called the atomic or fragment deformation energy, which corresponds to a combination of the traditional promotion energy and other effects, like spin-recoupling, true electronic deformation, etc.⁴ We have shown that the IQA interaction energies behave as *in situ* bond energies. IQA thus provides an invariant decomposition of the energy into group deformations and bond contributions in which covalent and ionic energies acquire rather pure forms.

1.2 The electron-counting face of bonding: Electron Distribution Functions

Electron counting provides access to the more qualitative view of chemical bonding in which the number of electrons engaged in sharing or in pure transfer between atoms gives rise to bonding descriptors like bond orders. In real space we simply examine the distribution of the electron population in the atomic regions in which we have divided the space.

EDFs are defined as follow. Given an N -electron molecule and an exhaustive partition of the real space (\mathcal{R}^3) into m arbitrary regions $\Omega_1, \Omega_2, \dots, \Omega_m$ ($\Omega_1 \cup \Omega_2 \cup \dots \cup \Omega_m = \mathcal{R}^3$), an EDF is the distribution function formed by all the probabilities $p(n_1, n_2, \dots, n_m)$ of finding exactly n_1 electrons in Ω_1 , n_2 electrons in Ω_2 , \dots , and n_m electrons in Ω_m , $\{n_p\}$ being integers ($n_i \in \mathcal{N}$) satisfying $n_1 + n_2 + \dots + n_m = N$. This view is in accord with considering subsystems as open quantum systems in which number operators do not commute with the subsystem hamiltonian. In this way, Ψ is not an eigenstate of the operator defining the number of electrons in domain Ω_i , \hat{N}_{Ω_i} . This means that the average number of electrons in Ω_i is not an eigenvalue of \hat{N}_{Ω_i} , so that measuring the number of electrons in the domain will render values n_{Ω_i} ranging from 0 to N , the total number of electrons, with a defined set of probabilities, $p(n_{\Omega_1})$. This is the one-fragment EDF for domain Ω_i . To obtain these probabilities or, in general, the multivariate electron distribution functions $p(n_1, n_2, \dots, n_m)$, one needs $\Psi(1, \dots, N)$, Ψ being the complete wave function,

$$p(n_1, n_2, \dots, n_m) = N! \Lambda \int_D \Psi^* \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_N, \quad (3)$$

where D is a multidimensional domain in which the first n_1 electrons are integrated over Ω_1 , the second n_2 electrons over Ω_2 , \dots , and the last n_m electrons over Ω_m , and $N! \Lambda = N! / (n_1! n_2! \cdots n_m!)$ is a combinatorial factor that accounts for electron indistinguishability. The 3D domains of these integrations can be arbitrary, but when using QTAIM atomic basins, a partition of the N electrons of the molecule that assigns a given number of electrons (including possibly 0) to each of these regions will be called a *real space resonance structure* (RSRS)⁵ and there are $N_S = (N + m - 1)! / [N!(m - 1)!]$ of these for a given N, m pair. With the notation $S(n_1, n_2, \dots, n_m) \equiv S(\{n_p\})$, or simply $(n_1, n_2, \dots, n_m) \equiv \{n_p\}$, we label the resonance structure having n_1 electrons in Ω_1 , n_2 electrons in Ω_2 , \dots , and n_m electrons in Ω_m . If electrons are spin-segregated, then we come to spin-resolved EDFs, and a set of probabilities $p(n_1^\alpha, n_1^\beta, n_2^\alpha, n_2^\beta, \dots, n_m^\alpha, n_m^\beta)$ which gives extremely fine-grained information about how electrons and their spins distribute.⁶

The computation of $p(n_1, n_2, \dots, n_m)$ for all the RSRSs provides all the statistical moments of the electron populations, including the average number of electrons in a given region, or its fluctuation. The average population is obviously given by

$$N_i = \langle n_i \rangle = \sum_{\{n_p\}} n_i \times p(\{n_p\}) = \sum_{n_i} n_i p_i(n_i). \quad (4)$$

It is not difficult to show that the number of shared pairs between two regions may be obtained directly by counting the number of intra- and interpairs.⁷ This has given rise to the so-called localization and delocalization indices, $(\lambda^{ii}, \delta^{ij})$, which determine the number of *localized* and *delocalized* pairs. The latter, which is the covalent bond-order in real space can be obtained from the $p(\{n_p\})$ probabilities as

$$\delta^{ij} = -2\text{cov}(i, j) = -2[\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle] = \quad (5)$$

$$-2 \left[\sum_{\{n_p\}} n_i n_j \times p(\{n_p\}) - \langle n_i \rangle \langle n_j \rangle \right] = \quad (6)$$

$$-2 \sum_{n_i n_j} (n_i - N_i)(n_j - N_j) p(n_i, n_j) = 2N_{ij} \quad (7)$$

where the -2 factor has been included to comply with the usual definition of δ in terms of the exchange-correlation density and to ensure that the bond order for an ideal single bond is equal to 1,

$$\delta^{ij} = -2 \int_{\Omega_i} \int_{\Omega_j} d\mathbf{1} d\mathbf{2} \rho_{xc}(1, 2). \quad (8)$$

The localization index is given by

$$\lambda_{ii} = N_i - \text{cov}(i, i) = N_i - \text{var}(i) = N_i - \sum_{n_i} (n_i - N_i)^2 p(n_i) = N_{ii} \quad (9)$$

From equations 5-9 it is clear that $N_{ii} = N_i$ if the variance is zero and that $N_{ij} = 0$ if the covariance is zero. This is the starting point for a complete theory of chemical bonding based on the fluctuation of electron populations. There is chemical bonding between two regions if their electron populations are not statistically independent. A sum rule, that classifies electrons into localized and delocalized sets appears:

$$N = \sum_{\Omega_i} N_i = \sum_{\Omega_i} \lambda^{ii} + \frac{1}{2} \sum_{\Omega_i \neq \Omega_j} \delta^{ij}. \quad (10)$$

Suitable generalizations in the case of multi-center bonding exist.⁸

1.3 Ionic and covalent structures in 2c-2e bonds

The statistical link between the fluctuation of electron populations and the standard energetic and bond order descriptors allows to map all coarse-grained (i.e. condensed at the atomic level) possible $(2c - 2e)$ bonds through simple models. In a two-center, two-electron system there are only three RSRs: $(2, 0)$, $(1, 1)$, $(0, 2)$, where we label how many electrons lie in each of the a, b domains. The central structure is obviously identified with the valence-bond covalent structure, while the other two describe ionic distributions. The EDF space is two-dimensional, since $p(2, 0) + p(1, 1) + p(0, 2) = 1$, and all bond indices become fully mapped in this 2D space. A convenient coordinate system can be built with the probability that any of the electrons lie in one of the basins, e.g. the left one, which we call p and provides a measure of heteropolarity, and a correlation factor $-1 \leq f \leq 1$ that determines how the electronic motion is correlated. $f = 1$ means that an electron is completely excluded from one domain if the other is already in it (positive correlation) and $f = -1$ implies that the two electrons are always found together within the same domain (negative correlation). The correlation factor here defined plays the same role as that used in density matrix theory, where $\rho^2(r_1, r_2) = \rho(r_1)\rho(r_2)(1 - f)$. The (p, f) pair describes fully a 2c,2e link at this level: $p(2, 0) = p^2 - p(1 - p)f$, $p(1, 1) = 2p(1 - p)(1 + f)$ and $p(0, 2) = (1 - p)^2 - p(1 - p)f$.⁹

If we use these p, f parameters, the covalent bond order becomes $\delta = 4p(1 - p)(1 - f)$. An ionic bond order $\iota = -Q_a Q_b$ where Q is the net charge of a center has also been defined.¹⁰

In standard weakly correlated bonds with positive $f \sim 0$, the EDF is close to binomial, and δ peaks at $\delta = 1$ for a purely covalent homopolar link with $p = 1/2$. As electron correlation, f , or polarity, p , increases δ decreases. Moreover, for non-correlated links with $f = 0$ $\iota = 1 - \delta$ so, in agreement with standard wisdom, the ionic and covalent bond orders are inversely correlated.

When f deviates from zero, the model describes positively or negatively correlated bonds. The latter case implies a bosonization of the link. Electrons try to delocalize together, giving rise to very large fluctuations. The most extreme 2c,2e case with $\delta = 2$ occurs when $p(0, 2) = p(2, 0) = 1/2$ and $p(1, 1) = 0$, i.e. when there is a resonance between the two non-orthogonal valence bond (NOVB) ionic structures. Thus, $f < 0$ serves to separate cleanly, in real space, large fluctuations from the standard bonding regime.

Several rigorous bond-energy bond-order (BEBO)¹⁰ relations can be uncovered using these real space descriptors. Under the IQA perspective a multipolar expansions shows that the first order ionic and covalent energies are immediately related to their corresponding bond orders. For an interaction between atoms A and B ,

$$E_{ion}^{AB} \sim -\frac{\iota^{AB}}{R_{ij}} \quad E_{cov}^{AB} \sim -\frac{1}{2} \frac{\delta^{AB}}{R_{AB}}. \quad (11)$$

Notice that the arguments posed in Section 3 show that in the absence of ionic contributions (delocalization) a system is unbound. This means, for instance, that the good behavior of the conventional covalent Heitler-London function of H_2 is due to the large overlap of the H 1s functions, that introduce a considerable amount of *real space ionic* terms.

1.4 Local spin

Spin densities have been used for almost three quarters of a century to understand the distribution of spin (and magnetism) in molecular systems. However, the spin density for a singlet state is identically zero everywhere, so that a question remains on how to quantify and localize spins in antiferromagnetic systems, or in singlet di- or polyradicals in molecules. This quest leads to the concept of local spin.

The expectation value of the $\langle \hat{S}^2 \rangle$ operator for an arbitrary N -electron molecular system described by the wave function Ψ can be expressed as

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \frac{3}{4} \int \rho(\mathbf{r}_1) d\mathbf{r}_1 \\ &+ \iint \left[-\frac{1}{4} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) \right] d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (12)$$

where $\rho(\mathbf{r}_1)$ is the electron density at point \mathbf{r}_1 and $\rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ is the spinless diagonal second-order density, normalized to N and $N(N-1)$, respectively. Considering the Dirac representation $\hat{S}^2 = -N(N-4)/4 + \hat{O}$, where $\hat{O} = \sum_{i < j} \hat{p}_{ij}^\sigma$ and \hat{p}_{ij}^σ is the operator interchanging the spin coordinates of electrons i and j , the first two terms in eq 12 add to $-N(N-4)/4$ and the second one is $\langle \Psi | \hat{O} | \Psi \rangle = -\frac{1}{2} \int \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$.

The concept of local spin answers the question of how to distribute $\langle \hat{S}^2 \rangle$ in atomic, $\langle \hat{S}^2 \rangle_A$, and inter-atomic contributions, $\langle \hat{S}^2 \rangle_{AB}$, in such a way that

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A \neq B} \langle \hat{S}^2 \rangle_{AB}, \quad (13)$$

where A and B run over all the atoms of the system or, in general, over the different groups of atoms in which the molecule has been divided. This can generally be done by assigning atomic projectors, as done by Clark and Davidson.¹¹ We thus define atomic regions, in our case using

the QTAIM, and define the one-electron projector for electron i as $P_A(i) = 1$ if $i \in \Omega_A$ and $P_A(i) = 0$ if $i \notin \Omega_A$, where Ω_A is the QTAIM atomic basin associated to atom A (that we will simply call A from now on). With this definition,

$$\langle \hat{S}_A^2 \rangle = \frac{3}{4} \int_A \rho(\mathbf{r}_1) d\mathbf{r}_1 + \int_A \int_A F(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (14)$$

$$\langle \hat{\mathbf{S}}_A \cdot \mathbf{S}_B \rangle = \int_A \int_B F(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad \text{where} \quad (15)$$

$$F(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{4} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \rho^2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1). \quad (16)$$

This provides a fully consistent partition of the squared spin operator into atomic and interatomic coupling terms. A fully isolated unpaired electron will offer a value for its local spin equal to $3/4$. As this delocalizes, the local spin will quench. In this sense, spin quenching and electron delocalization are fruitfully coupled together.

For instance, in the case of a single determinant closed-shell wavefunction (SDW),

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1; \mathbf{r}_1) \rho(\mathbf{r}_2; \mathbf{r}_2) - \frac{1}{2} \rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1), \quad \text{and} \quad (17)$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) = \rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1) - \frac{1}{2} \rho(\mathbf{r}_1; \mathbf{r}_1) \rho(\mathbf{r}_2; \mathbf{r}_2), \quad (18)$$

so that

$$-\frac{1}{4} \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_2, \mathbf{r}_1) = -\frac{3}{8} \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1). \quad (19)$$

Then,

$$\langle S^2 \rangle = \frac{3}{4} \int \rho(\mathbf{r}) d\mathbf{r} - \frac{3}{8} \int \int \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2. \quad (20)$$

The localization index inside A is given by

$$\lambda^A = \int_A \int_A \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (21)$$

where ρ_{xc} is the exchange-correlation density. Since, $\rho_{xc}(\mathbf{r}_1; \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1; \mathbf{r}_2) \rho(\mathbf{r}_2; \mathbf{r}_1)$ in the case of a closed-shell SDW, eq 14 becomes

$$\langle S_A^2 \rangle = \frac{3}{4} (N_A - \lambda_A), \quad (22)$$

where $N_A = \int \rho(\mathbf{r}) d\mathbf{r}$ is the average number on electron in A . Similarly, the delocalization index between A and B (δ^{AB}), a measure of the bond order between both atoms, is given by

$$\delta^{AB} = 2 \int_A \int_B \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (23)$$

and, from eqs 15, 16, and 19, its value for a closed-shell SDW is related to $\langle S_{AB}^2 \rangle$ by

$$\langle S_{AB}^2 \rangle = -\frac{3}{8} \delta^{AB}. \quad (24)$$

In the case of a $2c, 2e$ pure single bond with $\delta = 1$, this means that the local spin of each center will be quenched from $3/4$ to $3/8$, and that the spin coupling will change from $-3/4$ to $-3/8$. We have shown that there is an intimate relationship between local spins and electron distributions.¹² For instance in the symmetric $2c, 2e$ case with $p(2, 0) = p(0, 2) = 1/4$, the local spin of each center will be due to the resonance structure where each electron is located in a center, since when the two ionic configurations will lead to null $\langle S_A^2 \rangle$. Since $p(1, 1) = 1/2$ the local spin is $1/2 \times 3/4 = 3/8$. This EDF perspective is extremely fruitful. For two localized isolated spins coupled to a triplet, $\langle S_A^2 \rangle = 3/4$ and $\langle S_{AB}^2 \rangle = 1/4$.

2 The Coulson-Fischer state and its real space analysis

Let us consider a system with two equivalent centers (a,b) and two magnetic electrons. Two localized functions ϕ_a, ϕ_b (or just a, b) with overlap $\langle a|b \rangle = S$ are used. As stated in the manuscript, two ${}^1\Sigma_g^+$ singlets and one ${}^3\Sigma_u^+$ triplet come out from this basis. In the Heitler-London or Valence Bond (VB) framework, they are

$$\Psi_{S,cov} = \frac{1}{\sqrt{2(1+S^2)}}(a(1)b(2) + b(1)a(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow), \quad (25)$$

$$\Psi_{S,ion} = \frac{1}{\sqrt{2(1+S^2)}}(a(1)a(2) + b(1)b(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow). \quad (26)$$

$$\Psi_T = \frac{1}{\sqrt{2(1-S^2)}}(a(1)b(2) - b(1)a(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow). \quad (27)$$

Similarly, the MO basis is formed from the *gerade* and *ungerade* combinations, ϕ_g, ϕ_u (or simply g, u)

$$g = \frac{1}{\sqrt{2(1+S)}}(a+b), \quad u = \frac{1}{\sqrt{2(1-S)}}(a-b), \quad (28)$$

so that two independent ${}^1\Sigma_g^+$ singlets are:

$$\Psi_{gg} = \Psi_{HF} = |g\bar{g}\rangle, \quad \Psi_{uu} = |u\bar{u}\rangle. \quad (29)$$

while the ${}^3\Sigma_u^+$ triplet ($M_S = 0$ component) is given by

$$\Psi_T = \frac{1}{\sqrt{2}}(|g\bar{u}\rangle - |u\bar{g}\rangle). \quad (30)$$

The variational space of the singlets is two dimensional, so that the lowest energy singlet can be written as

$$\Psi_S = c\Psi_{cov} + i\Psi_{ion} = \lambda\Psi_{gg} + \mu\Psi_{uu}. \quad (31)$$

The $\lambda^2 + \mu^2 = 1$ condition allows to map easily the full spectrum of the singlets by using a ω -angle polar representation such that $\lambda = \cos(\omega/2)$, $\mu = -\sin(\omega/2)$, $\omega \in [-\pi, \pi]$.

Localized orthogonal Coulson-Fischer orbitals can be obtained from the localized a, b functions as $\varphi_{a,b} = (g \pm u)/\sqrt{2}$. With them, the Heitler-London-like Coulson-Fischer singlet state is obtained as the covalent function in Eq. 25. In terms of the g, u functions,

$$\Psi_S^o = \frac{1}{\sqrt{2}}(|g\bar{g}\rangle - |u\bar{u}\rangle). \quad (32)$$

The triplet built with this localized orthogonal functions (OLOs) is equal to the the canonical one.

Working in the orthogonal λ, μ representation provides direct easy access to all reduced density matrices. For the singlets, the $|g\bar{g}\rangle$ and $|u\bar{u}\rangle$ determinants differ in two spinorbitals, so only the 2RDM has coupling terms,

$$\begin{aligned} \rho(\mathbf{r}; \mathbf{r}') &= 2\lambda^2 g(\mathbf{r})g(\mathbf{r}') + 2\mu^2 u(\mathbf{r})u(\mathbf{r}') \\ \rho_2(\mathbf{r}_1, \mathbf{r}_2) &= 2\lambda^2 g^2(\mathbf{r}_1)g^2(\mathbf{r}_2) + 2\mu^2 u^2(\mathbf{r}_1)u^2(\mathbf{r}_2) + 4\lambda\mu gu(\mathbf{r}_1)gu(\mathbf{r}_2). \end{aligned} \quad (33)$$

Similarly, for the triplet

$$\begin{aligned} \rho(\mathbf{r}; \mathbf{r}') &= g(\mathbf{r})g(\mathbf{r}') + u(\mathbf{r})u(\mathbf{r}') \\ \rho_2(\mathbf{r}_1, \mathbf{r}_2) &= g^2(\mathbf{r}_1)u^2(\mathbf{r}_2) + u^2(\mathbf{r}_1)g^2(\mathbf{r}_2) - 2gu(\mathbf{r}_1)gu(\mathbf{r}_2). \end{aligned} \quad (34)$$

Since in Ψ_S^0 $\lambda = -\mu = 1/\sqrt{2}$, the first order density matrix of the Coulson-Fischer singlet and triplet are equal, and the pair densities differ in

$$\Delta\rho_2(\mathbf{r}_1, \mathbf{r}_2)_{S,T} = (g^2(\mathbf{r}_1) - u^2(\mathbf{r}_1))(g^2(\mathbf{r}_2) - u^2(\mathbf{r}_2)), \quad (35)$$

which can be written as $2\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_2)$. Notice that this difference integrates to zero.

For a two electron system the probability of finding the two electrons in a given atomic basin is given by

$$p(2, 0) = \frac{1}{2} \int_{\Omega} d\mathbf{r}_1 \int_{\Omega} d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2), \quad (36)$$

and given that the orthogonality of φ_a and φ_b also implies that $\int_{\Omega} \varphi_a(\mathbf{r})\varphi_b(\mathbf{r}) = 0$, then $p(2, 0)$ is equal for the Coulson-Fischer singlet and triplet, and so are $p(1, 1)$ and the variances and covariances (localization and delocalization indices).

The Coulson-Fischer singlet and triplet states can thus not be distinguished by any one-electron property or even by the atomic condensed electron distribution functions. Only when $\Delta\rho_2$ is weighted with the inverse interelectron distance to form the ΔV_{ee} operator we obtain an overall energy difference. This points clearly to a different average separation of electrons in both states, as shown in Fig. 1 of the ms.

3 Methodological details

All calculations in the H-X-H $^{n+}$ systems with X=He,Be and $n = 0, 2$ have been performed with the STO-6G minimal and the extended 6-311G(p) Pople basis sets at the Hartree-Fock (HF) and Full Configuration Interaction (FCI) levels with the **GAMESS** code.¹³ Calculations on the Li-Be-Li system were also performed with **GAMESS** and the 6-311+G** basis set.

In H-He-H we also substituted the He atom by an effective core potential, written with the following algebraic structure¹⁴:

$$V_{\text{eff}} = V_L(r) + \sum_{\lambda=0}^{L-1} \sum_{\mu=-\lambda}^{\lambda} |Y_{\lambda\mu}\rangle V_{\lambda-L}(r) \langle Y_{\lambda\mu}|, \quad (37)$$

$$V_{\lambda-L}(r) = V_{\lambda}(r) - V_L(r). \quad (38)$$

Here, $L-1$ is the maximum angular momentum of the excluded core electrons, and the $l = \lambda - L$ dependent V 's impose orthogonality constraints that avoid the collapse of the valence orbitals onto the bridge (core) states. The spherical harmonics and radial functions are centered at the He nucleus, and the $V_l(r)$ potentials are expressed as linear combinations of gaussians:

$$V_l(r) = \sum_{i=1}^N B_i^l r^{n_i^l} \exp(-\alpha_i^l r^2). \quad (39)$$

Here we have decided to use $L = 1$, so the ECP is a sum of a P potential and a S-P one. The B_i , n_i , and α_i coefficients are given in the following table:

n_i	B_i	n_i	α_i
P			
1	-0.11866700	2	0.80780000
2	-1.21779400	2	2.55000001
3	-1.37580501	1	7.25349998
S-P			
1	24.33369899	2	0.79980000
2	-20.66639709	2	0.77410000
3	-1.14289200	1	1.19430000
4	2.99401900	0	2.19990000

All real space analyses have been performed with our QTAIM in-house codes. IQA decompositions with PROMOLDEN, EDF probabilities with EDF, and local spin partitions with NRDM. They are freely available from the authors upon request, by writing to either ampendas@uniovi.es or evelio@uniovi.es. IQA integrations were performed using β -spheres with a radius 90% as large as the smallest atomic QTAIM bonded radius of each atom, with 434 and 5810 angular Lebedev points inside and outside the sphere, respectively, maximum l expansions up to $l = 10$, 4 outside and inside, respectively, and 700 and 400 trapezoidal and Gauss-Chebyshev radial points in the same order.

4 Raw Results

We offer here a list of results for the systems explored. We show the FCI 6-311G(p) data for H-He-H. Atomic numbering is always 1 for He and 2,3 for H atoms except for EDFs, in which the central He atom is atom 2. All data in atomic units. Geometries, canonical orbital energies and natural orbital occupations, main coefficients (> 0.01) of the FCI determinant expansion in the canonical basis with positive/negative labels tagging alpha and beta spin projections, IQA descriptors, EDF and local spin decompositions are found in consecutive order.

4.1 H-He-H LS

ATOM	ATOMIC CHARGE	COORDINATES (BOHR)		
		X	Y	Z
HE	2.0	0.0000000000	0.0000000000	0.0000000000
H	1.0	0.0000000000	0.0000000000	-2.3786536587
H	1.0	0.0000000000	0.0000000000	2.3786536587

EIGENVECTORS

1	2	3	4	5
-1.0556	-0.3124	-0.0269	0.3836	0.3928
AG	B1U	AG	AG	B1U

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

1	2	3	4	5
1.9818	1.4942	0.5044	0.0066	0.0039
AG	B1U	AG	AG	B1U

TOTAL ENERGY = -3.8327720116

ELECTRON-ELECTRON POTENTIAL ENERGY = 2.6522763715

NUCLEUS-ELECTRON POTENTIAL ENERGY = -12.3468267482
 NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.8918264891

 TOTAL POTENTIAL ENERGY = -7.8027238875
 TOTAL KINETIC ENERGY = 3.9699518760
 VIRIAL RATIO (V/T) = 1.9654454591

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.8600731486E+00	1	2	-1	-2
-0.4983389596E+00	1	3	-1	-3
-0.3999934103E-01	2	4	-2	-4
-0.2852488019E-01	2	6	-2	-6
-0.2852488019E-01	2	7	-2	-7
-0.2779527407E-01	2	3	-2	-4
-0.2779527407E-01	2	4	-2	-3
0.2267670752E-01	3	4	-3	-4
-0.2105905507E-01	2	5	-2	-5
-0.1999847491E-01	2	3	-2	-3
-0.1681461010E-01	1	5	-1	-5
0.1674848128E-01	3	7	-3	-7
0.1674848128E-01	3	6	-3	-6
0.1669365677E-01	1	8	-2	-3
0.1669365677E-01	2	3	-1	-8
-0.1549172969E-01	1	2	-3	-5
-0.1549172969E-01	3	5	-1	-2
0.1425802262E-01	3	5	-3	-5
0.1239230589E-01	1	3	-2	-8
0.1239230589E-01	2	8	-1	-3
0.1122241557E-01	1	9	-2	-5
0.1122241557E-01	2	5	-1	-9
-0.1070696621E-01	1	9	-1	-9
-0.1031310282E-01	1	8	-1	-8

Atomic Contributions for neq: 1
 Atom number : 1

kinetic energy	=	2.90411770			
potential energy	=	-5.73496917			
electron repulsion	=	1.05361204			
---coulomb	=	2.07270320			
---exch+corr	=	-1.01909116			
---self	=	0.00000000			
el-own-nuc attraction	=	-6.72888677			
net energy	=	-2.77115703			
interaction energy	=	-0.11938889			
additive energy	=	-2.83085148			
effective energy	=	-2.89054592			
2T+V	=	0.07326622			
Int rho_2	=	2.28136968			
Integ rho_2 J	=	4.04937901			
Integ rho_2 XC (F_AA)	=	1.76800933			
SUM-RULE-TEST	=	2.01224996	AND SHOULD BE	2.01230689	
=====	Interaction with atom:	2	=====		
(NN,EN,NE,EE,Inter)	0.84081177	-0.83720355	-0.72925369	0.66595102	-0.05969444
EE wself : (coul,XC,self)	0.72837773	-0.06242671	0.00000000		
EE woself: (coul,XC)	0.72837773	-0.06242671			
Coul comp.: (longr, shortr)	-0.342826E+03	0.343554E+03			
Classical Int. (Long,Total)	-0.343673E+03	0.273227E-02			
RHO_2 Integ comp (TOT,J,XC)	1.87763990	1.99976022	0.12212032		

F_AB (XC) 0.24424063

```
===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.84081177 -0.83720355 -0.72925369 0.66595102 -0.05969444
EE wself : (coul,XC,self) 0.72837773 -0.06242671 0.00000000
EE woself: (coul,XC) 0.72837773 -0.06242671
Coul comp.: (longr, shortr) -0.342826E+03 0.343554E+03
Classical Int. (Long,Total) -0.343673E+03 0.273227E-02
RHO_2 Integ comp (TOT,J,XC) 1.87763990 1.99976022 0.12212032
F_AB (XC) 0.24424063
Atomic Contributions for neq: 2
  Atom number : 2
```

```
-----
kinetic energy = 0.53283705
potential energy = -1.03382920
electron repulsion = 0.04462788
---coulomb = 0.33016294
---exch+corr = -0.28553507
---self = 0.00000000
el-own-nuc attraction = -1.04598508
net energy = -0.46852015
interaction energy = -0.06494400
additive energy = -0.50099215
effective energy = -0.53346415
2T+V = 0.03184490
Int rho_2 = 0.15718711
Integ rho_2 J = 0.98756894
Integ rho_2 XC (F_AA) = 0.83038183
SUM-RULE-TEST = 0.99371196 AND SHOULD BE 0.99376503
```

```
===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.21020294 -0.19640851 -0.19640851 0.17736451 -0.00524956
EE wself : (coul,XC,self) 0.18442648 -0.00706197 0.00000000
EE woself: (coul,XC) 0.18442648 -0.00706197
Coul comp.: (longr, shortr) 0.185393E+00 -0.966655E-03
Classical Int. (Long,Total) 0.273221E-02 0.181241E-02
RHO_2 Integ comp (TOT,J,XC) 0.94635913 0.98756894 0.04120981
F_AB (XC) 0.08241962
```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```
#-----
# NUMBER OF GROUPS = 3
# TOTAL NUMBER OF PROBABILITIES = 15
#-----
```

#	Probability	n1(H)	n2(He)	n3(H)
#	0.7278283855326309	1	2	1
#	0.0570771504525981	1	3	0
#	0.0570771504525981	0	3	1
#	0.0528440664176910	2	1	1
#	0.0528440664176910	1	1	2
#	0.0228116412268904	2	2	0
#	0.0228116412268904	0	2	2
#	0.0041089204834032	0	4	0
#	0.0014400237727642	2	0	2
#	0.0002728138540450	3	1	0
#	0.0002728138540450	0	1	3
#	0.0002237579192957	1	0	3
#	0.0002237579192957	3	0	1
#	0.0000003780052079	0	0	4
#	0.0000003780052079	4	0	0

Average populations and localization indices

```

# <n( 1)> = 0.9936560505
# <n( 2)> = 2.0120356812
# <n( 3)> = 0.9936560505
# <n( 2) n( 1)> = 1.8774854281
# <n( 3) n( 1)> = 0.9463072938
# <n( 3) n( 2)> = 1.8774854281
# <n( 3) n( 2) n( 1)> = 1.6670330367
# delta_( 1 1) = 0.8301769172 % Localization = 83.5477
# delta_( 2 2) = 1.7671513951 % Localization = 87.8290
# delta_( 3 3) = 0.8301769172 % Localization = 83.5477

```

Delocalization indices

```

# delta_( 2 1) = 0.2442239808
# delta_( 3 1) = 0.0824120902
# delta_( 3 2) = 0.2442239808
# delta_( 3 2 1) = 0.0107594207

```

```

# Fragment A formed by atoms 1: He
# Fragment B formed by atoms 2 3: H, H

```

```

# -----
# < S_A^2 > = 0.19782118, < S_AB^2 > = -0.19777624
# rho^1(r1;r1) part = 1.50923016, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.57034241, rho^2(r1,r2;r1,r2) part = -0.93881994
# rho^2(r1,r2;r2,r1) part = -0.74106657, rho^2(r1,r2;r2,r1) part = 0.74104370
# < S_B^2 > = 0.19785360
# rho^1(r1;r1) part = 1.49064754
# rho^2(r1,r2;r1,r2) part = -0.55177311
# rho^2(r1,r2;r2,r1) part = -0.74102083

```

```

# -----
# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3

```

```

# -----
# < S_A^2 > = 0.66278284, < S_AB^2 > = -0.66274417
# rho^1(r1;r1) part = 0.74532377, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.03929677, rho^2(r1,r2;r1,r2) part = -0.70599975
# rho^2(r1,r2;r2,r1) part = -0.04324415, rho^2(r1,r2;r2,r1) part = 0.04325559
# < S_B^2 > = 0.66282778
# rho^1(r1;r1) part = 2.25455393
# rho^2(r1,r2;r1,r2) part = -1.54845913
# rho^2(r1,r2;r2,r1) part = -0.04326702
# -----

```

4.2 H-He-H LT

ATOM	ATOMIC CHARGE	COORDINATES (BOHR)		
		X	Y	Z
HE	2.0	0.0000000000	0.0000000000	0.0000000000
H	1.0	0.0000000000	0.0000000000	-2.3786536587
H	1.0	0.0000000000	0.0000000000	2.3786536587

EIGENVECTORS

```

-----
1 2 3 4 5

```

-0.9513	-0.1854	-0.0994	0.2801	0.3266
AG	B1U	AG	AG	B1U

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

1	2	3	4	5
1.9832	0.9993	0.9992	0.0067	0.0029
AG	AG	B1U	AG	B1U

TOTAL ENERGY = -3.8116308380

ELECTRON-ELECTRON POTENTIAL ENERGY = 2.6368800561

NUCLEUS-ELECTRON POTENTIAL ENERGY = -12.4305485252

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.8918264891

TOTAL POTENTIAL ENERGY = -7.9018419800

TOTAL KINETIC ENERGY = 4.0902111420

VIRIAL RATIO (V/T) = 1.9318909723

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.7033287160E+00	1	2	-1	-3
-0.7033287160E+00	1	3	-1	-2
-0.3242931340E-01	2	4	-3	-4
0.3242931340E-01	3	4	-2	-4
-0.2360802682E-01	2	6	-3	-6
0.2360802682E-01	3	6	-2	-6
-0.2360802682E-01	2	7	-3	-7
0.2360802682E-01	3	7	-2	-7
0.2054077032E-01	2	3	-2	-4
-0.2054077032E-01	2	4	-2	-3
-0.2039663467E-01	2	5	-3	-5
0.2039663467E-01	3	5	-2	-5
0.2025185335E-01	1	8	-2	-3
-0.2025185335E-01	2	3	-1	-8
0.1425105024E-01	1	4	-3	-4
-0.1425105024E-01	3	4	-1	-4
0.1273827264E-01	1	4	-2	-3
-0.1273827264E-01	2	3	-1	-4
0.1116495271E-01	1	3	-3	-9
-0.1116495271E-01	3	9	-1	-3
0.1015371523E-01	2	3	-3	-5
-0.1015371523E-01	3	5	-2	-3

Atomic Contributions for neq: 1

Atom number : 1

kinetic energy	=	3.01022302
potential energy	=	-5.84233420
electron repulsion	=	1.07085502
---coulomb	=	2.12538737
---exch+corr	=	-1.05453235
---self	=	0.00000000
el-own-nuc attraction	=	-6.86426410
net energy	=	-2.78318607
interaction energy	=	-0.09785023
additive energy	=	-2.83211118
effective energy	=	-2.88103630
2T+V	=	0.17811183

```

Int rho_2          =      2.27550726
Integ rho_2 J      =      4.08773618
Integ rho_2 XC    (F_AA) =      1.81222892
SUM-RULE-TEST     =      2.02179956  AND SHOULD BE      2.02181507
===== Interaction with atom:  2 =====
(NN,EN,NE,EE,Inter)      0.84081177   -0.83941034   -0.71619004   0.66586349   -0.04892512
EE wself : (coul,XC,self) 0.71766594   -0.05180245   0.00000000
EE woself: (coul,XC)      0.71766594   -0.05180245
Coul comp.: (longr, shorttr) -0.888970E+04  0.889042E+04
Classical Int. (Long,Total) -0.889066E+04  0.287734E-02
RHO_2 Integ comp (TOT,J,XC) 1.89495366   1.99973898   0.10478532
F_AB (XC)              0.20957064

```

```

===== Interaction with atom:  3 =====
(NN,EN,NE,EE,Inter)      0.84081177   -0.83941034   -0.71619004   0.66586349   -0.04892512
EE wself : (coul,XC,self) 0.71766594   -0.05180245   0.00000000
EE woself: (coul,XC)      0.71766594   -0.05180245
Coul comp.: (longr, shorttr) -0.888970E+04  0.889042E+04
Classical Int. (Long,Total) -0.889066E+04  0.287734E-02
RHO_2 Integ comp (TOT,J,XC) 1.89495366   1.99973898   0.10478532
F_AB (XC)              0.20957064
Atomic Contributions for neq:  2
  Atom number          :  2

```

```

-----
kinetic energy      =      0.53998101
potential energy    =     -1.02973254
electron repulsion  =      0.02745815
---coulomb         =      0.32369802
---exch+corr       =     -0.29623987
---self            =      0.00000000
el-own-nuc attraction =     -1.03332685
net energy          =     -0.46588769
interaction energy   =     -0.04772769
additive energy     =     -0.48975153
effective energy    =     -0.51361537
2T+V               =      0.05022948
Int rho_2          =      0.10089691
Integ rho_2 J      =      0.97828133
Integ rho_2 XC    (F_AA) =      0.87738442
SUM-RULE-TEST     =      0.98907743  AND SHOULD BE      0.98908106

```

```

===== Interaction with atom:  3 =====
(NN,EN,NE,EE,Inter)      0.21020294   -0.19418654   -0.19418654   0.17936756   0.00119743
EE wself : (coul,XC,self) 0.18046716   -0.00109960   0.00000000
EE woself: (coul,XC)      0.18046716   -0.00109960
Coul comp.: (longr, shorttr) 0.187049E+00 -0.658172E-02
Classical Int. (Long,Total) 0.874036E-02  0.229702E-02
RHO_2 Integ comp (TOT,J,XC) 0.97137365   0.97828133   0.00690768
F_AB (XC)              0.01381536

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS          =      3
# TOTAL NUMBER OF PROBABILITIES =     15
#-----
#   Probability             n1(H) n2(He) n3(H)
#   Probability             n1    n2    n3 ...
#   0.7918691748069808      1     2     1
#   0.0528771617903641      1     3     0

```

```

# 0.0528771617903641 0 3 1
# 0.0439858313864634 2 1 1
# 0.0439858313864634 1 1 2
# 0.0051051647318951 2 2 0
# 0.0051051647318951 0 2 2
# 0.0030670864319878 0 4 0
# 0.0006005387579096 2 0 2
# 0.0001907003446540 3 0 1
# 0.0001907003446540 1 0 3
# 0.0000612673807049 3 1 0
# 0.0000612673807049 0 1 3
# 0.0000000781913864 4 0 0
# 0.0000000781913864 0 0 4

```

Average populations and localization indices

```

# <n( 1)> = 0.9890621540
# <n( 2)> = 2.0217845225
# <n( 3)> = 0.9890621540
# <n( 2) n( 1)> = 1.8949317902
# <n( 3) n( 1)> = 0.9713588575
# <n( 3) n( 2)> = 1.8949317902
# <n( 3) n( 2) n( 1)> = 1.7596816752
# delta_( 1 1) = 0.8773481301 % Localization = 88.7051
# delta_( 2 2) = 1.8121226684 % Localization = 89.6299
# delta_( 3 3) = 0.8773481301 % Localization = 88.7051

```

Delocalization indices

```

# delta_( 2 1) = 0.2095686836
# delta_( 3 1) = 0.0138147671
# delta_( 3 2) = 0.2095686836
# delta_( 3 2 1) = 0.0060694926

```

```

# Fragment A formed by atoms 1: He
# Fragment B formed by atoms 2 3: H, H

```

```

# -----
# < S_A^2 > = 0.18069652, < S_AB^2 > = -0.01183974
# rho^1(r1;r1) part = 1.51636131, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.56887683, rho^2(r1,r2;r1,r2) part = -0.94747684
# rho^2(r1,r2;r2,r1) part = -0.76678796, rho^2(r1,r2;r2,r1) part = 0.93563710
# < S_B^2 > = 1.84298955
# rho^1(r1;r1) part = 1.48362159
# rho^2(r1,r2;r1,r2) part = -0.53613529
# rho^2(r1,r2;r2,r1) part = 0.89550326
# -----

```

```

# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3

```

```

# -----
# < S_A^2 > = 0.71233306, < S_AB^2 > = 0.20324185
# rho^1(r1;r1) part = 0.74181080, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.02522423, rho^2(r1,r2;r1,r2) part = -0.71658184
# rho^2(r1,r2;r2,r1) part = -0.00425351, rho^2(r1,r2;r2,r1) part = 0.91982369
# < S_B^2 > = 0.88118984
# rho^1(r1;r1) part = 2.25817211
# rho^2(r1,r2;r1,r2) part = -1.54157790
# rho^2(r1,r2;r2,r1) part = 0.16459563

```

4.3 H-He-H BS

ATOM	ATOMIC CHARGE	COORDINATES (BOHR)		
		X	Y	Z
HE	2.0	0.0000000000	0.0000000000	1.6629588692
H	1.0	0.0000000000	-1.7007533889	0.0000000000
H	1.0	0.0000000000	1.7007533889	0.0000000000

EIGENVECTORS

	1	2	3	4	5
	-1.0754	-0.2854	-0.0639	0.3661	0.3980
	A1	B2	A1	A1	B2

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	1.9837	1.1700	0.8282	0.0069	0.0028
	A1	A1	B2	A1	B2

TOTAL ENERGY = -3.8102031609

ELECTRON-ELECTRON POTENTIAL ENERGY = 2.7273896090

NUCLEUS-ELECTRON POTENTIAL ENERGY = -12.6211262778

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.9756107487

TOTAL POTENTIAL ENERGY = -7.9181259201

TOTAL KINETIC ENERGY = 4.1079227592

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.7359975185E+00	1	3	-1	-3
-0.6288086818E+00	1	2	-1	-2
-0.1336656226E+00	1	3	-1	-4
-0.1336656226E+00	1	4	-1	-3
0.6975657511E-01	1	2	-1	-5
0.6975657511E-01	1	5	-1	-2
0.3673587766E-01	1	2	-2	-3
0.3673587766E-01	2	3	-1	-2
-0.2731375808E-01	3	6	-3	-6
0.2590922013E-01	2	6	-2	-6
-0.2479618149E-01	1	2	-1	-9
-0.2479618149E-01	1	9	-1	-2
-0.2038016853E-01	1	3	-1	-6
-0.2038016853E-01	1	6	-1	-3
0.1822969654E-01	1	4	-1	-4
-0.1756747238E-01	3	7	-3	-7
-0.1702480265E-01	1	5	-2	-3
-0.1702480265E-01	2	3	-1	-5
-0.1569720429E-01	3	9	-3	-9
0.1469947170E-01	2	7	-2	-7
-0.1412878076E-01	2	3	-2	-6
-0.1412878076E-01	2	6	-2	-3
-0.1410968807E-01	1	3	-1	-8
-0.1410968807E-01	1	8	-1	-3
0.1347012778E-01	2	9	-2	-9
-0.1308559822E-01	3	8	-3	-8
0.1288258920E-01	1	6	-3	-6
0.1288258920E-01	3	6	-1	-6
0.1248318944E-01	1	3	-1	-15
0.1248318944E-01	1	15	-1	-3

```

0.1072337844E-01  2  8  -2  -8
-0.1055932944E-01  1  2  -1 -17
-0.1055932944E-01  1 17  -1  -2
-0.1043358411E-01  3  7  -3 -12
-0.1043358411E-01  3 12  -3  -7
0.1030524333E-01  1  3  -1 -16
0.1030524333E-01  1 16  -1  -3
-0.1007802751E-01  3 18  -3 -18
-0.1007698826E-01  1  3  -3  -6
-0.1007698826E-01  3  6  -1  -3

```

```

Atomic Contributions for neq:  1
      Atom number           :  1

```

```

-----
kinetic energy      =      3.023375
potential energy    =     -5.857378
electron repulsion  =      1.086185
---coulomb         =              2.150206
---exch+corr       =     -1.064021
---self            =              0.000000
el-own-nuc attraction =     -6.896778
net energy          =     -2.787218
interaction energy  =     -0.093570
additive energy     =     -2.834003
effective energy    =     -2.880788
2T+V               =      0.189372
Int rho_2          =      2.311886
Integ rho_2 J      =      4.153317
Integ rho_2 XC (F_AA) =      1.841431
SUM-RULE-TEST      =      2.038148  AND SHOULD BE      2.037969

```

```

===== Interaction with atom:  2 =====
(NN,EN,NE,EE,Inter)      0.840812   -0.846554   -0.713477   0.672434   -0.046785
EE wself : (coul,XC,self)  0.720980   -0.048546   0.000000
EE woself: (coul,XC)      0.720980   -0.048546
Coul comp.: (longr, short) 0.346699E+04 -0.346627E+04
Classical Int. (Long,Total) 0.346614E+04 0.176086E-02
RHO_2 Integ comp (TOT,J,XC) 1.904443   2.002801   0.098358
F_AB (XC)                 0.196717

```

```

===== Interaction with atom:  3 =====
(NN,EN,NE,EE,Inter)      0.840812   -0.846554   -0.713477   0.672434   -0.046785
EE wself : (coul,XC,self)  0.720980   -0.048546   0.000000
EE woself: (coul,XC)      0.720980   -0.048546
Coul comp.: (longr, short) 0.346699E+04 -0.346627E+04
Classical Int. (Long,Total) 0.346614E+04 0.176086E-02
RHO_2 Integ comp (TOT,J,XC) 1.904443   2.002801   0.098358
F_AB (XC)                 0.196717

```

```

Atomic Contributions for neq:  2
      Atom number           :  2

```

```

-----
kinetic energy      =      0.543184
potential energy    =     -1.031005
electron repulsion  =      0.031910
---coulomb         =              0.323982
---exch+corr       =     -0.292072
---self            =              0.000000
el-own-nuc attraction =     -1.035377
net energy          =     -0.460282
interaction energy  =     -0.055077

```

```

additive energy          =      -0.487820
effective energy         =      -0.515359
2T+V                    =       0.055364
Int rho_2                =       0.117284
Integ rho_2 J           =       0.965785
Integ rho_2 XC (F_AA)  =       0.848501
SUM-RULE-TEST           =       0.984384 AND SHOULD BE       0.982744
===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)    0.293987      -0.269114      -0.269114      0.235950      -0.008291
EE wself : (coul,XC,self) 0.249083      -0.013133      0.000000
EE woself: (coul,XC)     0.249083      -0.013133
Coul comp.: (longr, shortr) 0.219897E+01 -0.194989E+01
Classical Int. (Long,Total) 0.195125E+01 0.484184E-02
RHO_2 Integ comp (TOT,J,XC) 0.928261      0.965785      0.037524
F_AB (XC)               0.075049

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS          =       3
# TOTAL NUMBER OF PROBABILITIES =     15
#-----
#   Probability           n1    n2    n3 ...
#   0.7791971178074078    1     2     1
#   0.0537289978792667    0     3     1
#   0.0537289978792667    1     3     0
#   0.0364381367233987    1     1     2
#   0.0364381367233987    2     1     1
#   0.0192109648824038    2     2     0
#   0.0192109648824038    0     2     2
#   0.0032618146468190    0     4     0
#   0.0006536988810710    3     1     0
#   0.0006536988810710    0     1     3
#   0.0006345519702162    2     0     2
#   0.0001498992468092    1     0     3
#   0.0001498992468092    3     0     1
#   0.0000021432112770    0     0     4
#   0.0000021432112770    4     0     0

```

Average populations and delocalization indices

```

# <n( 1)>          =      0.9845008260
# <n( 2)>          =      2.0448430122
# <n( 3)>          =      0.9845008260
# <n( 2) n( 1)>    =      1.9077005956
# <n( 3) n( 1)>    =      0.9283872681
# <n( 3) n( 2)>    =      1.9077005956
# <n( 3) n( 2) n( 1)> =    1.7041467825
# delta_( 1 1)    =      0.8518272620 % Localization = 86.5238
# delta_( 2 2)    =      1.8622550992 % Localization = 91.0708
# delta_( 3 3)    =      0.8518272620 % Localization = 86.5238
# delta_( 2 1)    =      0.1969623877
# delta_( 3 1)    =      0.0749998026
# delta_( 3 2)    =      0.1969623877
# delta_( 3 2 1)  =      0.0130200950

```

```

# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3
#-----

```

```

# < S_A^2 > =      0.15403963,      < S_AB^2 > =      -0.15426755
# rho^1(r1;r1) part =      1.52847654, rho^1(r1;r1) part =      0.00000000

```



```

# rho^2(r1,r2;r1,r2) part = -0.57797140, rho^2(r1,r2;r1,r2) part = -0.95222136
# rho^2(r1,r2;r2,r1) part = -0.79646551, rho^2(r1,r2;r2,r1) part = 0.79795381
# < S_B^2 > = 0.15189605
# rho^1(r1;r1) part = 1.47411564
# rho^2(r1,r2;r1,r2) part = -0.52277271
# rho^2(r1,r2;r2,r1) part = -0.79944689
# -----
# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3
# -----
# < S_A^2 > = 0.69033136, < S_AB^2 > = -0.69151711
# rho^1(r1;r1) part = 0.73705782, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.02932109, rho^2(r1,r2;r1,r2) part = -0.70817594
# rho^2(r1,r2;r2,r1) part = -0.01740537, rho^2(r1,r2;r2,r1) part = 0.01665884
# < S_B^2 > = 0.69010344
# rho^1(r1;r1) part = 2.26553437
# rho^2(r1,r2;r1,r2) part = -1.55951386
# rho^2(r1,r2;r2,r1) part = -0.01591707

```

4.4 H-He-H BT

ATOM	ATOMIC CHARGE	COORDINATES (BOHR)		
		X	Y	Z
HE	2.0	0.0000000000	0.0000000000	1.6629588692
H	1.0	0.0000000000	-1.7007533889	0.0000000000
H	1.0	0.0000000000	1.7007533889	0.0000000000

EIGENVECTORS

	1	2	3	4	5
	-0.9526	-0.1585	-0.1286	0.2929	0.3222
	A1	A1	B2	A1	B2

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	1.9830	0.9993	0.9989	0.0071	0.0028
	A1	A1	B2	A1	A1

TOTAL ENERGY = -3.8143631935

ELECTRON-ELECTRON POTENTIAL ENERGY = 2.7116381747

NUCLEUS-ELECTRON POTENTIAL ENERGY = -12.5804293330

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.9756107487

TOTAL POTENTIAL ENERGY = -7.8931804096

TOTAL KINETIC ENERGY = 4.0788172161

VIRIAL RATIO (V/T) = 1.9351640418

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.7031431599E+00	1	2	-1	-3
-0.7031431599E+00	1	3	-1	-2
-0.2764695850E-01	2	6	-3	-6
0.2764695850E-01	3	6	-2	-6
0.1659919446E-01	2	3	-2	-6
-0.1659919446E-01	2	6	-2	-3
-0.1495770357E-01	1	4	-2	-3

0.1495770357E-01	2	3	-1	-4
-0.1417148789E-01	2	9	-3	-9
0.1417148789E-01	3	9	-2	-9
-0.1367153292E-01	2	8	-3	-8
0.1367153292E-01	3	8	-2	-8
-0.1348775998E-01	1	2	-2	-3
0.1348775998E-01	2	3	-1	-2
0.1127877017E-01	2	13	-3	-8
-0.1127877017E-01	3	8	-2	-13
0.1126510053E-01	2	8	-3	-13
-0.1126510053E-01	3	13	-2	-8
-0.1113156367E-01	2	7	-3	-7
0.1113156367E-01	3	7	-2	-7
-0.1092395670E-01	2	13	-3	-13
0.1092395670E-01	3	13	-2	-13
0.1073820145E-01	2	3	-2	-7
-0.1073820145E-01	2	7	-2	-3
0.1017998312E-01	1	7	-2	-3
-0.1017998312E-01	2	3	-1	-7
0.1016883214E-01	1	6	-3	-6
-0.1016883214E-01	3	6	-1	-6

Atomic Contributions for neq: 1
 Atom number : 1

```

-----
kinetic energy      =      2.983151
potential energy    =     -5.814969
electron repulsion  =      1.066818
---coulomb         =              2.114995
---exch+corr       =     -1.048177
---self            =              0.000000
el-own-nuc attraction =     -6.831300
net energy          =     -2.781331
interaction energy  =     -0.100974
additive energy     =     -2.831817
effective energy    =     -2.882304
2T+V               =      0.151334
Int rho_2          =      2.286201
Integ rho_2 J      =      4.100018
Integ rho_2 XC (F_AA) =      1.813817
SUM-RULE-TEST      =      2.025150  AND SHOULD BE      2.024850
===== Interaction with atom:  2 =====
(NN,EN,NE,EE,Inter)      0.840812   -0.842270   -0.720139   0.671110   -0.050487
EE wself : (coul,XC,self) 0.723792   -0.052682   0.000000
EE woself: (coul,XC)      0.723792   -0.052682
Coul comp.: (longr, shortr) 0.208813E+04 -0.208741E+04
Classical Int. (Long>Total) 0.208727E+04 0.219483E-02
RHO_2 Integ comp (TOT,J,XC) 1.897011   2.002677   0.105666
F_AB (XC)                0.211332
===== Interaction with atom:  3 =====
(NN,EN,NE,EE,Inter)      0.840812   -0.842270   -0.720139   0.671110   -0.050487
EE wself : (coul,XC,self) 0.723792   -0.052682   0.000000
EE woself: (coul,XC)      0.723792   -0.052682
Coul comp.: (longr, shortr) 0.208813E+04 -0.208741E+04
Classical Int. (Long>Total) 0.208727E+04 0.219483E-02
RHO_2 Integ comp (TOT,J,XC) 1.897011   2.002677   0.105666
F_AB (XC)                0.211332
Atomic Contributions for neq: 2

```

```

Atom number      : 2
-----
kinetic energy   =      0.548753
potential energy =     -1.039705
electron repulsion =      0.033061
---coulomb      =              0.328917
---exch+corr    =     -0.295856
---self         =      0.000000
el-own-nuc attraction =     -1.044443
net energy       =     -0.462630
interaction energy =     -0.056645
additive energy  =     -0.490952
effective energy =     -0.519275
2T+V            =      0.057800
Int rho_2       =      0.124451
Integ rho_2 J   =      0.978219
Integ rho_2 XC (F_AA) =      0.853768
SUM-RULE-TEST   =      0.990378 AND SHOULD BE      0.989049
===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.293987 -0.269720 -0.269720 0.239295 -0.006158
EE wself : (coul,XC,self) 0.250043 -0.010748 0.000000
EE woself: (coul,XC) 0.250043 -0.010748
Coul comp.: (longr, shortr) 0.159259E+01 -0.134255E+01
Classical Int. (Long,Total) 0.134420E+01 0.458975E-02
RHO_2 Integ comp (TOT,J,XC) 0.947275 0.978219 0.030944
F_AB (XC) 0.061888

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS = 3
# TOTAL NUMBER OF PROBABILITIES = 15
#-----
# Probability      n1   n2   n3   ...
# 0.7713682927334732 1    2    1
# 0.0536763809816437 0    3    1
# 0.0536763809816437 1    3    0
# 0.0432743923083669 1    1    2
# 0.0432743923083669 2    1    1
# 0.0160798162434760 0    2    2
# 0.0160798162434760 2    2    0
# 0.0034020001643794 0    4    0
# 0.0006255404391828 0    1    3
# 0.0006255404391828 3    1    0
# 0.0004993336137804 2    0    2
# 0.0001814183507976 3    0    1
# 0.0001814183507976 1    0    3
# 0.0000022621629189 0    0    4
# 0.0000022621629189 4    0    0
#-----
# 1.0029492474844048 <-- SUM, 15 PROBABILITIES > 0.0000000000E+00
# 1.0029492474844048 <--- TOTAL SUM
#-----

```

Average populations and delocalization indices

```

# <n( 1)> = 0.9906374937
# <n( 2)> = 2.0305220025
# <n( 3)> = 0.9906374937
# <n( 2) n( 1)> = 1.8997847916

```

```

# <n( 3) n( 1)>      =      0.9475517065
# <n( 3) n( 2)>      =      1.8997847916
# <n( 3) n( 2) n( 1)> =      1.7158341547
# delta_( 1 1)      =      0.8567866610 % Localization = 86.4884
# delta_( 2 2)      =      1.8310231784 % Localization = 90.1750
# delta_( 3 3)      =      0.8567866610 % Localization = 86.4884
# delta_( 2 1)      =      0.2115879829
# delta_( 3 1)      =      0.0618333123
# delta_( 3 2)      =      0.2115879829
# delta_( 3 2 1)    =      0.0145869141

# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3
# -----
#          < S_A^2 > =      0.18287681,          < S_AB^2 > =      -0.00693111
# rho^1(r1;r1)      part =      1.51863753, rho^1(r1;r1)      part =      0.00000000
# rho^2(r1,r2;r1,r2) part =      -0.57155013, rho^2(r1,r2;r1,r2) part =      -0.94850533
# rho^2(r1,r2;r2,r1) part =      -0.76421059, rho^2(r1,r2;r2,r1) part =      0.94157423
#          < S_B^2 > =      1.83431331
# rho^1(r1;r1)      part =      1.48357421
# rho^2(r1,r2;r1,r2) part =      -0.53586282
# rho^2(r1,r2;r2,r1) part =      0.88660192
# -----
# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3
# -----
#          < S_A^2 > =      0.71698130,          < S_AB^2 > =      0.19670980
# rho^1(r1;r1)      part =      0.74178711, rho^1(r1;r1)      part =      0.00000000
# rho^2(r1,r2;r1,r2) part =      -0.03111267, rho^2(r1,r2;r1,r2) part =      -0.71107140
# rho^2(r1,r2;r2,r1) part =      0.00630686, rho^2(r1,r2;r2,r1) part =      0.90778121
#          < S_B^2 > =      0.89292700
# rho^1(r1;r1)      part =      2.26042464
# rho^2(r1,r2;r1,r2) part =      -1.55116813
# rho^2(r1,r2;r2,r1) part =      0.18367050

```

4.5 ECP H-He-H LS

Geometries as in the non-ECP calculations. With only two electrons, the EDF and its statistics is immediately found from the delocalization index (F_{AB}) as follows: $p(2,0) = p(0,2) = (1 - p(1,1))/2 = 4\delta^{AB}$. Similarly, the local spin is given by $\langle S_A^2 \rangle = 3/4p(1,1)$.

EIGENVECTORS

```

          1          2          3          4          5
      -0.1654   -0.0778   0.4185   0.4500   1.5480
          A1          B2          B2          A1          B1

```

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

```

          1          2          3          4          5
      1.4510   0.5483   0.0004   0.0001   0.0001
          B2          A1          B2          A2          B2

```

```

TOTAL ENERGY =      -0.8928014429

```

```

ELECTRON-ELECTRON POTENTIAL ENERGY =      0.2177511601
NUCLEUS-ELECTRON POTENTIAL ENERGY =      -2.5006221754
NUCLEUS-NUCLEUS POTENTIAL ENERGY =      0.2102029432

```

```

-----
TOTAL POTENTIAL ENERGY =      -2.0726680720
TOTAL KINETIC ENERGY =       1.1798666291
VIRIAL RATIO (V/T) =         1.7566969189

```

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

```

0.8517493642E+00  1  -1
-0.5236001813E+00  2  -2
-0.1362173454E-01  3  -3

```

```

Atomic Contributions for neq:  1
Atom number      :  1

```

```

-----
kinetic energy      =      0.58992811
potential energy    =     -1.05939246
electron repulsion  =      0.01699221
---coulomb          =              0.33826471
---exch+corr        =             -0.32127251
---self             =              0.00000000
el-own-nuc attraction =     -1.06995214
net energy          =     -0.46303182
interaction energy   =     -0.01286505
additive energy     =     -0.46946435
effective energy    =     -0.47589687
2T+V                =      0.12046377
Int rho_2           =      0.07274313
Integ rho_2 J       =      0.99999470
Integ rho_2 XC (F_AA) =     0.92725157
SUM-RULE-TEST       =      0.99999472  AND SHOULD BE      0.99999735

```

```

===== Interaction with atom:  2 =====
(NN,EN,NE,EE,Inter)      0.21020294  -0.20341748  -0.20341748  0.18376697  -0.01286505
EE wself : (coul,XC,self)  0.19711680  -0.01334983  0.00000000
EE woself: (coul,XC)       0.19711680  -0.01334983
Coul comp.: (longr, short) 0.197121E+00 -0.456006E-05
Classical Int. (Long,Total) 0.482538E-03 0.484783E-03
RHO_2 Integ comp (TOT,J,XC) 0.92725156  0.99999470  0.07274315
F_AB (XC)                 0.14548629

```

4.6 ECP H-He-H LT

EIGENVECTORS

	1	2	3	4	5
	-0.4836	-0.3925	0.3699	0.4175	1.5099
	B2	A1	B2	A1	A1

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	1.0000	1.0000	0.0000	0.0000	0.0000
	A1	B2	A1	B2	A1

ENERGY COMPONENTS

```

WAVEFUNCTION NORMALIZATION =      1.0000000000
      ONE ELECTRON ENERGY =      -1.2815485671
      TWO ELECTRON ENERGY =       0.2026393777
      NUCLEAR REPULSION ENERGY =    0.2102029432
-----
      TOTAL ENERGY =             -0.8687062461
ELECTRON-ELECTRON POTENTIAL ENERGY =    0.2026393777
NUCLEUS-ELECTRON POTENTIAL ENERGY =   -2.5231354914
NUCLEUS-NUCLEUS POTENTIAL ENERGY =    0.2102029432
-----
      TOTAL POTENTIAL ENERGY =   -2.1102931704
      TOTAL KINETIC ENERGY =     1.2415869243
      VIRIAL RATIO (V/T) =        1.6996741260

```

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

```

0.7070999672E+00  2  -1
-0.7070999672E+00  1  -2

```

```

Atomic Contributions for neq:  1
      Atom number      :  1

```

```

-----
kinetic energy      =      0.62078857
potential energy    =     -1.10487732
electron repulsion  =      0.00264444
---coulomb          =           0.35071604
---exch+corr        =          -0.34807160
---self             =           0.00000000
el-own-nuc attraction =    -1.10598972
net energy          =    -0.48255670
interaction energy   =    -0.00306407
additive energy     =    -0.48408874
effective energy    =    -0.48562078
2T+V                =      0.13669983
Int rho_2           =      0.01386589
Integ rho_2 J       =      0.99999117
Integ rho_2 XC (F_AA) =    0.98612528
SUM-RULE-TEST       =    0.99999118  AND SHOULD BE    0.99999559

```

```

===== Interaction with atom:  2 =====
(NN,EN,NE,EE,Inter)      0.21020294  -0.20530843  -0.20530843  0.19734985  -0.00306407
EE wself : (coul,XC,self)  0.20067145  -0.00332160  0.00000000
EE woself: (coul,XC)      0.20067145  -0.00332160
Coul comp.: (longr, shortr) 0.200695E+00 -0.230803E-04
Classical Int. (Long,Total) 0.274087E-03 0.257525E-03
RHO_2 Integ comp (TOT,J,XC) 0.98612527  0.99999117  0.01386590
F_AB (XC)                0.02773180

```

4.7 ECP H-He-H BS

EIGENVECTORS

	1	2	3	4	5
	-0.2499	-0.0022	0.4281	0.4345	1.3896
	A1	B2	A1	B2	A1

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	1.0327	0.9669	0.0002	0.0001	0.0000
	A1	B2	A1	B2	A1

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.000000000

ONE ELECTRON ENERGY = -1.4340876090

TWO ELECTRON ENERGY = 0.2734222305

NUCLEAR REPULSION ENERGY = 0.2939873607

TOTAL ENERGY = -0.8666780178

ELECTRON-ELECTRON POTENTIAL ENERGY = 0.2734222305

NUCLEUS-ELECTRON POTENTIAL ENERGY = -2.6839433550

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 0.2939873607

TOTAL POTENTIAL ENERGY = -2.1165337637

TOTAL KINETIC ENERGY = 1.2498557459

VIRIAL RATIO (V/T) = 1.6934224374

Atomic Contributions for neq: 1
 Atom number : 1

kinetic energy	=	0.624923		
potential energy	=	-1.105488		
electron repulsion	=	0.008944		
---coulomb	=		0.352979	
---exch+corr	=		-0.344035	
---self	=		0.000000	
el-own-nuc attraction	=	-1.109037		
net energy	=	-0.475170		
interaction energy	=	-0.010791		
additive energy	=	-0.480565		
effective energy	=	-0.485960		
2T+V	=	0.144358		
Int rho_2	=	0.036110		
Integ rho_2 J	=	0.999986		
Integ rho_2 XC (F_AA)	=	0.963875		
SUM-RULE-TEST	=	0.999986	AND SHOULD BE	0.999993

===== (NN,EN,NE,EE,Inter)	0.293987	-0.280166	-0.280166	0.255554	-0.010791
EE wself : (coul,XC,self)	0.267904	-0.012350	0.000000		
EE woself: (coul,XC)	0.267904	-0.012350			
Coul comp.: (longr, shortr)	0.285827E+00	-0.179230E-01			
Classical Int. (Long,Total)	0.190804E-01	0.155964E-02			
RHO_2 Integ comp (TOT,J,XC)	0.963875	0.999986	0.036110		
F_AB (XC)	0.072221				

4.8 ECP H-He-H BT

EIGENVECTORS

	1	2	3	4	5
	-0.4609	-0.4336	0.3670	0.3947	1.3248
	A1	B2	B2	A1	A1

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	0.9997	0.9997	0.0002	0.0002	0.0000
	B2	A1	A1	B2	B2

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.000000000

ONE ELECTRON ENERGY = -1.434235455

TWO ELECTRON ENERGY = 0.2690934408

NUCLEAR REPULSION ENERGY = 0.2939873607

TOTAL ENERGY = -0.8711547440

ELECTRON-ELECTRON POTENTIAL ENERGY = 0.2690934408

NUCLEUS-ELECTRON POTENTIAL ENERGY = -2.6702806335

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 0.2939873607

TOTAL POTENTIAL ENERGY = -2.1071998319

TOTAL KINETIC ENERGY = 1.2360450880

VIRIAL RATIO (V/T) = 1.7047920439

Atomic Contributions for neq: 1
 Atom number : 1

kinetic energy	=	0.61801769		
potential energy	=	-1.09913696		
electron repulsion	=	0.00854069		
---coulomb	=	0.35005433		
---exch+corr	=	-0.34151364		
---self	=	0.00000000		
el-own-nuc attraction	=	-1.10112054		
net energy	=	-0.47456216		
interaction energy	=	-0.01311422		
additive energy	=	-0.48111927		
effective energy	=	-0.48767638		
2T+V	=	0.13689841		
Int rho_2	=	0.04186221		
Integ rho_2 J	=	0.99998558		
Integ rho_2 XC (F_AA)	=	0.95812338		
SUM-RULE-TEST	=	0.99998558	AND SHOULD BE	0.99999279

===== (NN,EN,NE,EE,Inter)	Interaction with atom: 2	0.29398736	-0.27955661	-0.27955661	0.25201165	-0.01311422
EE wself : (coul,XC,self)		0.26675464	-0.01474299	0.00000000		
EE woself: (coul,XC)		0.26675464	-0.01474299			
Coul comp.: (longr, shortr)		0.267090E+00	-0.335654E-03			
Classical Int. (Long,Total)		0.184414E-02	0.162877E-02			


```

RHO_2 Integ comp (TOT,J,XC)      0.95812337    0.99998558    0.04186221
F_AB (XC)                        0.08372441

```

4.9 H-Be-H²⁺ LS

Geometries and numbering as in the H-He-H calculations.

```

-----
EIGENVECTORS
-----

```

```

          1          2          3          4          5
      -5.4896   -1.1090   -0.8619   -0.4743   -0.4743
          AG      B1U      AG      B3U      B2U
NATURAL ORBITALS IN ATOMIC ORBITAL BASIS
-----

```

```

          1          2          3          4          5
      1.9983     1.0447     0.9535     0.0013     0.0007
          AG      AG      B1U      AG      B3U
-----

```

```

-----
ENERGY COMPONENTS
-----

```

```

WAVEFUNCTION NORMALIZATION =      1.0000000000

```

```

ONE ELECTRON ENERGY =      -22.7109881842

```

```

TWO ELECTRON ENERGY =      4.4845840301

```

```

NUCLEAR REPULSION ENERGY =      3.5734500350
-----

```

```

TOTAL ENERGY =      -14.6529541190

```

```

ELECTRON-ELECTRON POTENTIAL ENERGY =      4.4845840301

```

```

NUCLEUS-ELECTRON POTENTIAL ENERGY =     -37.8530165005

```

```

NUCLEUS-NUCLEUS POTENTIAL ENERGY =      3.5734500350
-----

```

```

TOTAL POTENTIAL ENERGY =     -29.7949824353

```

```

TOTAL KINETIC ENERGY =      15.1420283163

```

```

VIRIAL RATIO (V/T) =      1.9677008795

```

```

Atomic Contributions for neq:  1

```

```

Atom number      :  1
-----

```

```

kinetic energy    =      14.01091799

```

```

potential energy  =     -27.78808508

```

```

electron repulsion =      2.62242813

```

```

---coulomb        =      4.95642945

```

```

---exch+corr      =     -2.33400132

```

```

---self           =      0.00000000

```

```

el-own-nuc attraction =     -30.39070938

```

```

net energy        =     -13.75736326

```

```

interaction energy =     -0.03960765

```

```

additive energy   =     -13.77716708

```

```

effective energy  =     -13.79697091

```

```

2T+V              =      0.23375091

```

```

Int rho_2         =      2.80234226

```

```

Integ rho_2 J     =      4.80917236

```

```

Integ rho_2 XC (F_AA) =      2.00683010

```

```

SUM-RULE-TEST    =      2.19298556  AND SHOULD BE      2.19298253

```

```

===== Interaction with atom:  2 =====

```

```

(NN,EN,NE,EE,Inter)      1.68162354   -0.91900066   -1.61576395   0.83333723   -0.01980382

```

```

EE wself : (coul,XC,self)      0.88318239   -0.04984516   0.00000000
EE woself: (coul,XC)          0.88318239   -0.04984516
Coul comp.: (longr, shorttr)  0.581699E+00  0.301483E+00
Classical Int. (Long,Total)  -0.288440E+00  0.300413E-01
RHO_2 Integ comp (TOT,J,XC)   1.88834987    1.98142760    0.09307773
F_AB (XC)                      0.18615546

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)          1.68162354   -0.91900066   -1.61576395    0.83333723   -0.01980382
EE wself : (coul,XC,self)      0.88318239   -0.04984516   0.00000000
EE woself: (coul,XC)          0.88318239   -0.04984516
Coul comp.: (longr, shorttr)  0.581699E+00  0.301483E+00
Classical Int. (Long,Total)  -0.288440E+00  0.300413E-01
RHO_2 Integ comp (TOT,J,XC)   1.88834987    1.98142760    0.09307773
F_AB (XC)                      0.18615546
Atomic Contributions for neq: 2
  Atom number                   : 2

```

```

-----
kinetic energy      =      0.56556243
potential energy    =     -1.00342083
electron repulsion  =      0.00381273
---coulomb         =           0.30132833
---exch+corr       =          -0.29751560
---self            =           0.00000000
el-own-nuc attraction =     -0.99651542
net energy          =     -0.42714026
interaction energy   =     -0.02143628
additive energy     =     -0.43785840
effective energy    =     -0.44857654
2T+V                =      0.12770403
Int rho_2           =      0.01472889
Integ rho_2 J       =      0.81636819
Integ rho_2 XC (F_AA) =      0.80163931
SUM-RULE-TEST      =      0.90355168  AND SHOULD BE      0.90353096

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)          0.21020294   -0.19995566   -0.19995566    0.18807593   -0.00163245
EE wself : (coul,XC,self)      0.19052262   -0.00244669   0.00000000
EE woself: (coul,XC)          0.19052262   -0.00244669
Coul comp.: (longr, shorttr)  0.190526E+00 -0.341065E-05
Classical Int. (Long,Total)  0.797824E-03  0.814242E-03
RHO_2 Integ comp (TOT,J,XC)   0.80753355    0.81636819    0.00883464
F_AB (XC)                      0.01766929

```

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

```

 0.7224233093E+00  1  2 -1 -2
-0.6901499037E+00  1  3 -1 -3
-0.1730925646E-01  2  4 -2 -4
-0.1729894884E-01  1  6 -1 -6
-0.1729894884E-01  1  5 -1 -5
 0.1660246313E-01  3  4 -3 -4
 0.1297446546E-01  1  7 -1 -7

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS           =      3
# TOTAL NUMBER OF PROBABILITIES =     15
#-----
#   Probability              n1   n2   n3 ...

```

```

# 0.7955322188862616      2      1      1
# 0.0903557769930355      3      0      1
# 0.0903557769930355      3      1      0
# 0.0091551200670438      4      0      0
# 0.0043139690496871      2      0      2
# 0.0043139690496871      2      2      0
# 0.0029850245554108      1      1      2
# 0.0029850245554108      1      2      1
# 0.0000157444703766      1      0      3
# 0.0000157444703766      1      3      0
# 0.0000117368815215      0      2      2
# 0.0000021636222075      0      1      3
# 0.0000021636222075      0      3      1
# 0.0000000119755672      0      0      4
# 0.0000000119755672      0      4      0
#-----
# 1.0000444571673964 <-- SUM,      15 PROBABILITIES > 0.0000000000E+00
# 1.0000444571673964 <--- TOTAL SUM
#-----

```

Average populations and localization indices

```

# <n( 1)> = 2.1930769942
# <n( 2)> = 0.9035504172
# <n( 3)> = 0.9035504172
# <n( 2) n( 1)> = 1.8883899520
# <n( 3) n( 1)> = 1.8883899520
# <n( 3) n( 2)> = 0.8075322464
# <n( 3) n( 2) n( 1)> = 1.6030045360
# delta_( 1 1) = 2.0071356240 % Localization = 91.5214
# delta_( 2 2) = 0.8016743032 % Localization = 88.7249
# delta_( 3 3) = 0.8016743032 % Localization = 88.7249

```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```

# delta_( 2 1) = 0.1861551735
# delta_( 3 1) = 0.1861551735
# delta_( 3 2) = 0.0176696302
# delta_( 3 2 1) = 0.0006086535

```

```

# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3

```

```

#-----
# < S_A^2 > = 0.14218712, < S_AB^2 > = -0.14218912
# rho^1(r1;r1) part = 1.64473690, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.70058557, rho^2(r1,r2;r1,r2) part = -0.94417494
# rho^2(r1,r2;r2,r1) part = -0.80196420, rho^2(r1,r2;r2,r1) part = 0.80198583
# < S_B^2 > = 0.14215777
# rho^1(r1;r1) part = 1.35529645
# rho^2(r1,r2;r1,r2) part = -0.41113123
# rho^2(r1,r2;r2,r1) part = -0.80200745
#-----

```

```

# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3

```

```

#-----
# < S_A^2 > = 0.67101785, < S_AB^2 > = -0.67103352
# rho^1(r1;r1) part = 0.67764822, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.00368222, rho^2(r1,r2;r1,r2) part = -0.67397086
# rho^2(r1,r2;r2,r1) part = -0.00294815, rho^2(r1,r2;r2,r1) part = 0.00293734
# < S_B^2 > = 0.67101586

```

```

# rho^1(r1;r1)      part =      2.32238512
# rho^2(r1,r2;r1,r2) part =     -1.64844274
# rho^2(r1,r2;r2,r1) part =     -0.00292653

```

4.10 H-Be-H²⁺ LT

Geometries as in the H-He-H calculations.

EIGENVECTORS

```

-----
1          2          3          4          5
-5.4849   -0.9843   -0.9736   -0.5385   -0.5385
AG         AG         B1U        B3U        B2U

```

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

```

-----
1          2          3          4          5
1.9983    0.9997    0.9997    0.0013    0.0003
AG         B1U        AG         AG         B1U

```

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -22.7170911725

TWO ELECTRON ENERGY = 4.4895756697

NUCLEAR REPULSION ENERGY = 3.5734500350

TOTAL ENERGY = -14.6540654677

ELECTRON-ELECTRON POTENTIAL ENERGY = 4.4895756697

NUCLEUS-ELECTRON POTENTIAL ENERGY = -37.8553860093

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 3.5734500350

TOTAL POTENTIAL ENERGY = -29.7923603045

TOTAL KINETIC ENERGY = 15.1382948368

VIRIAL RATIO (V/T) = 1.9680129516

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

```

0.7066912286E+00  1  2  -1  -3
-0.7066912286E+00  1  3  -1  -2
-0.1692623274E-01  2  4  -3  -4
0.1692623274E-01  3  4  -2  -4

```

Atomic Contributions for neq: 1

Atom number : 1

```

-----
kinetic energy      =      14.00707764
potential energy    =     -27.78596302
electron repulsion  =       2.62855557
---coulomb          =       4.96249742
---exch+corr        =     -2.33394185
---self             =       0.00000000
el-own-nuc attraction =    -30.39445338
net energy          =    -13.75882017

```

```

interaction energy      =      -0.04013043
additive energy        =     -13.77888539
effective energy        =     -13.79895060
2T+V                   =       0.22819225
Int rho_2              =       2.81470614
Integ rho_2 J          =       4.82213729
Integ rho_2 XC (F_AA) =       2.00743115
SUM-RULE-TEST          =       2.19595438  AND SHOULD BE  2.19593654

```

```

===== Interaction with atom: 2 =====
(NN,EN,NE,EE,Inter)   1.68162354  -0.92055270  -1.61424579  0.83310973  -0.02006521
EE wself : (coul,XC,self)  0.88382587  -0.05071614  0.00000000
EE woself: (coul,XC)     0.88382587  -0.05071614
Coul comp.: (longr, shortr) 0.653805E+00 0.230021E+00
Classical Int. (Long,Total) -0.217374E+00 0.306509E-01
RHO_2 Integ comp (TOT,J,XC) 1.88666867  1.98093029  0.09426162
F_AB (XC)               0.18852323

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)   1.68162354  -0.92055270  -1.61424579  0.83310973  -0.02006521
EE wself : (coul,XC,self)  0.88382587  -0.05071614  0.00000000
EE woself: (coul,XC)     0.88382587  -0.05071614
Coul comp.: (longr, shortr) 0.653805E+00 0.230021E+00
Classical Int. (Long,Total) -0.217374E+00 0.306509E-01
RHO_2 Integ comp (TOT,J,XC) 1.88666867  1.98093029  0.09426162
F_AB (XC)               0.18852323

```

```

Atomic Contributions for neq: 2
      Atom number      : 2

```

```

-----
kinetic energy          =       0.56565557
potential energy        =     -1.00323696
electron repulsion      =       0.00376560
---coulomb              =           0.30100904
---exch+corr            =          -0.29724343
---self                 =           0.00000000
el-own-nuc attraction   =     -0.99622292
net energy              =     -0.42680174
interaction energy       =     -0.02155930
additive energy         =     -0.43758139
effective energy        =     -0.44836104
2T+V                   =       0.12807418
Int rho_2              =       0.01486399
Integ rho_2 J          =       0.81376464
Integ rho_2 XC (F_AA) =       0.79890064
SUM-RULE-TEST          =       0.90213743  AND SHOULD BE  0.90208904

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)   0.21020294  -0.19966195  -0.19966195  0.18762688  -0.00149408
EE wself : (coul,XC,self)  0.18996233  -0.00233544  0.00000000
EE woself: (coul,XC)     0.18996233  -0.00233544
Coul comp.: (longr, shortr) 0.189970E+00 -0.776940E-05
Classical Int. (Long,Total) 0.828316E-03 0.841360E-03
RHO_2 Integ comp (TOT,J,XC) 0.80478946  0.81376464  0.00897517
F_AB (XC)               0.01795034

```

```

# M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

```

#-----
# NUMBER OF GROUPS      =       3
# TOTAL NUMBER OF PROBABILITIES =     15

```

```

#-----
#      Probability          n1    n2    n3 ...
#      0.7930079828771008    2     1     1
#      0.0913888664880521    3     1     0
#      0.0913888664880521    3     0     1
#      0.0095446035644586    4     0     0
#      0.0044370254155184    2     2     0
#      0.0044370254155184    2     0     2
#      0.0029322865466683    1     1     2
#      0.0029322865466683    1     2     1
#      0.0000150630514328    1     0     3
#      0.0000150630514328    1     3     0
#      0.0000112338045561    0     2     2
#      0.0000021489736564    0     1     3
#      0.0000021489736564    0     3     1
#      0.0000000111619125    0     0     4
#      0.0000000111619125    0     4     0
#-----
#      1.0001146235205965 <-- SUM,      15 PROBABILITIES > 0.0000000000E+00
#      1.0001146235205965 <--- TOTAL SUM
#-----

```

Average populations and localization indices

```

# <n( 1)>          =      2.1961703798
# <n( 2)>          =      0.9021440571
# <n( 3)>          =      0.9021440571
# <n( 2) n( 1)>    =      1.8867727157
# <n( 3) n( 1)>    =      1.8867727157
# <n( 3) n( 2)>    =      0.8047949581
# <n( 3) n( 2) n( 1)> =      1.5977451119
# delta_( 1 1)    =      2.0081986291 % Localization = 91.4409
# delta_( 2 2)    =      0.7989994022 % Localization = 88.5667
# delta_( 3 3)    =      0.7989994022 % Localization = 88.5667

```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```

# delta_( 2 1)    =      0.1885244834
# delta_( 3 1)    =      0.1885244834
# delta_( 3 2)    =      0.0179513075
# delta_( 3 2 1)  =      0.0011187633

```

```

# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3

```

```

#-----
#      < S_A^2 > =      0.16315830,      < S_AB^2 > =      0.04118535
# rho^1(r1;r1)   part =      1.64695240, rho^1(r1;r1)   part =      0.00000000
# rho^2(r1,r2;r1,r2) part =      -0.70367652, rho^2(r1,r2;r1,r2) part =      -0.94333434
# rho^2(r1,r2;r2,r1) part =      -0.78011758, rho^2(r1,r2;r2,r1) part =      0.98451969
#      < S_B^2 > =      1.75459940
# rho^1(r1;r1)   part =      1.35313357
# rho^2(r1,r2;r1,r2) part =      -0.40982674
# rho^2(r1,r2;r2,r1) part =      0.81129257
#-----

```

```

# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3

```

```

#-----
#      < S_A^2 > =      0.67795043,      < S_AB^2 > =      0.21994195
# rho^1(r1;r1)   part =      0.67656678, rho^1(r1;r1)   part =      0.00000000
# rho^2(r1,r2;r1,r2) part =      -0.00371600, rho^2(r1,r2;r1,r2) part =      -0.67286454
#-----

```

```

# rho^2(r1,r2;r2,r1) part =      0.00509964, rho^2(r1,r2;r2,r1) part =      0.89280649
#          < S_B^2 > =      0.88229408
# rho^1(r1;r1) part =      2.32351918
# rho^2(r1,r2;r1,r2) part =     -1.65072686
# rho^2(r1,r2;r2,r1) part =      0.20950175

```

4.11 H-Be-H²⁺ BS

Geometries as in the H-He-H calculations.

```

-----
EIGENVECTORS
-----

```

1	2	3	4	5
-5.4906	-1.2159	-0.7481	-0.5348	-0.4865
A1	A1	B2	A1	B1

```

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS
-----

```

1	2	3	4	5
1.9983	1.7001	0.2954	0.0020	0.0017
A1	A1	B2	B1	A1

```

-----
ENERGY COMPONENTS
-----

```

WAVEFUNCTION NORMALIZATION = 1.0000000000

ONE ELECTRON ENERGY = -22.9715887345

TWO ELECTRON ENERGY = 4.6272204239

NUCLEAR REPULSION ENERGY = 3.6572341367

TOTAL ENERGY = -14.6871341739

ELECTRON-ELECTRON POTENTIAL ENERGY = 4.6272204239

NUCLEUS-ELECTRON POTENTIAL ENERGY = -38.0696391062

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 3.6572341367

TOTAL POTENTIAL ENERGY = -29.7851845456

TOTAL KINETIC ENERGY = 15.0980503717

VIRIAL RATIO (V/T) = 1.9727834927

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

```

0.9215763307E+00  1  2  -1  -2
-0.3841070727E+00  1  3  -1  -3
-0.3096198864E-01  1  4  -1  -4
-0.2041054912E-01  1  5  -1  -5
-0.1478431488E-01  1  7  -1  -7
-0.1233077409E-01  2  6  -2  -6
-0.1158437744E-01  2  5  -2  -5
-0.1058556548E-01  1  6  -1  -6
-0.1001886360E-01  1  5  -1  -6
-0.1001886360E-01  1  6  -1  -5

```

```

Atomic Contributions for neq:  1
Atom number                   :  1

```

```

-----
kinetic energy      =      14.06220559
potential energy    =     -27.85133360
electron repulsion  =       2.63512042
---coulomb          =          4.97549250
---exch+corr        =         -2.34037208
---self             =          0.00000000
el-own-nuc attraction =   -30.46295166
net energy          =   -13.76562565
interaction energy   =    -0.04700472
additive energy     =   -13.78912801
effective energy     =   -13.81263037
2T+V                =     0.27307759
Int rho_2           =     2.83965784
Integ rho_2 J       =     4.85039168
Integ rho_2 XC      (F_AA) =     2.01073384
SUM-RULE-TEST       =     2.20251729  AND SHOULD BE     2.20236048

(NN,EN,NE,EE,Inter)      1.68162339  -0.92980600  -1.62017844   0.84485870  -0.02350236
EE wself : (coul,XC,self)  0.89651292  -0.05165422   0.00000000
EE woself: (coul,XC)      0.89651292  -0.05165422
Coul comp.: (longr, shortr) 0.244425E+01 -0.154774E+01
Classical Int. (Long,Total) 0.154307E+01  0.281519E-01
RHO_2 Integ comp (TOT,J,XC) 1.88556114   1.98145287   0.09589172
F_AB (XC)                 0.19178345

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)      1.68162339  -0.92980600  -1.62017844   0.84485870  -0.02350236
EE wself : (coul,XC,self)  0.89651292  -0.05165422   0.00000000
EE woself: (coul,XC)      0.89651292  -0.05165422
Coul comp.: (longr, shortr) 0.244425E+01 -0.154774E+01
Classical Int. (Long,Total) 0.154307E+01  0.281519E-01
RHO_2 Integ comp (TOT,J,XC) 1.88556114   1.98145287   0.09589172
F_AB (XC)                 0.19178345

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS          =          3
# TOTAL NUMBER OF PROBABILITIES =        15
#-----
#   Probability             n1    n2    n3 ...
#   0.6618412845069302      2     1     1
#   0.0940507148089871      3     0     1
#   0.0940507148089871      3     1     0
#   0.0683590981039454      2     0     2
#   0.0683590981039454      2     2     0
#   0.0098524964105640      4     0     0
#   0.0024258232090498      1     1     2
#   0.0024258232090498      1     2     1
#   0.0001879386233923      1     0     3
#   0.0001879386233923      1     3     0
#   0.0000063142801025      0     2     2
#   0.0000019637524668      0     1     3
#   0.0000019637524668      0     3     1
#   0.0000001240440137      0     4     0
#   0.0000001240440137      0     0     4
#-----
#   1.0017514202813068 <-- SUM,      15 PROBABILITIES > 0.0000000000E+00
#   1.0017514202813068 <--- TOTAL SUM

```


#-----

Average populations and localization indices

```
# <n( 1)> = 2.2060607596
# <n( 2)> = 0.9004724608
# <n( 3)> = 0.9004724608
# <n( 2) n( 1)> = 1.8871123914
# <n( 3) n( 1)> = 1.8871123914
# <n( 3) n( 2)> = 0.6715816170
# <n( 3) n( 2) n( 1)> = 1.3333858619
# delta_( 1 1) = 2.0227465789 % Localization = 91.6904
# delta_( 2 2) = 0.6681272786 % Localization = 74.1974
# delta_( 3 3) = 0.6681272786 % Localization = 74.1974
```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```
# delta_( 2 1) = 0.1918107567
# delta_( 3 1) = 0.1918107567
# delta_( 3 2) = 0.2756977907
# delta_( 3 2 1) = 0.0553784593
```

Fragment A formed by atoms 1

Fragment B formed by atoms 2 3

```
# -----
# < S_A^2 > = 0.14677591, < S_AB^2 > = -0.14692277
# rho^1(r1;r1) part = 1.65177036, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.70991446, rho^2(r1,r2;r1,r2) part = -0.94278057
# rho^2(r1,r2;r2,r1) part = -0.79507999, rho^2(r1,r2;r2,r1) part = 0.79585780
# < S_B^2 > = 0.14575543
# rho^1(r1;r1) part = 1.34954261
# rho^2(r1,r2;r1,r2) part = -0.40715073
# rho^2(r1,r2;r2,r1) part = -0.79663644
# -----
```

Fragment A formed by atoms 2

Fragment B formed by atoms 1 3

```
# -----
# < S_A^2 > = 0.57196324, < S_AB^2 > = -0.57254691
# rho^1(r1;r1) part = 0.67477130, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.03567993, rho^2(r1,r2;r1,r2) part = -0.63928572
# rho^2(r1,r2;r2,r1) part = -0.06712813, rho^2(r1,r2;r2,r1) part = 0.06673881
# < S_B^2 > = 0.57181639
# rho^1(r1;r1) part = 2.32654166
# rho^2(r1,r2;r1,r2) part = -1.68837496
# rho^2(r1,r2;r2,r1) part = -0.06635032
```

4.12 H-Be-H²⁺ BT

Geometries as in the H-He-H calculations.

EIGENVECTORS

1	2	3	4	5
-5.4983	-1.0475	-0.8903	-0.5589	-0.5336
A1	A1	B2	A1	B1

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	1.9983	0.9994	0.9994	0.0013	0.0004
	A1	A1	B2	A1	B2

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.000000000

ONE ELECTRON ENERGY = -22.8297106617

TWO ELECTRON ENERGY = 4.5387604490

NUCLEAR REPULSION ENERGY = 3.6572341367

TOTAL ENERGY = -14.6337160761

ELECTRON-ELECTRON POTENTIAL ENERGY = 4.5387604490

NUCLEUS-ELECTRON POTENTIAL ENERGY = -37.9724297646

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 3.6572341367

TOTAL POTENTIAL ENERGY = -29.7764351789

TOTAL KINETIC ENERGY = 15.1427191029

VIRIAL RATIO (V/T) = 1.9663862862

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.7065885946E+00	1	2	-1	-3
-0.7065885946E+00	1	3	-1	-2
-0.1722482824E-01	2	4	-3	-4
0.1722482824E-01	3	4	-2	-4

Atomic Contributions for neq: 1
 Atom number : 1

kinetic energy	=	13.96006762
potential energy	=	-27.72758991
electron repulsion	=	2.61175523
---coulomb	=	4.94133023
---exch+corr	=	-2.32957500
---self	=	0.00000000
el-own-nuc attraction	=	-30.32014048
net energy	=	-13.74831763
interaction energy	=	-0.03840932
additive energy	=	-13.76752229
effective energy	=	-13.78672695
2T+V	=	0.19254533
Int rho_2	=	2.78843946
Integ rho_2 J	=	4.79597920
Integ rho_2 XC (F_AA)	=	2.00753974

===== (NN,EN,NE,EE,Inter)	Interaction with atom:	2	===== 1.68162339	===== -0.92092286	===== -1.61501369	===== 0.83510850	===== -0.01920466
EE wself : (coul,XC,self)			0.88454053	-0.04943203	0.00000000		
EE woself: (coul,XC)			0.88454053	-0.04943203			
EE woself: (coul,XC)			0.88454053	-0.04943203			
Coul comp.: (longr, shortr)			0.950356E+00	-0.658157E-01			
Classical Int. (Long,Total)			0.881476E-01	0.302274E-01			
RHO_2 Integ comp (TOT,J,XC)			1.89432768	1.98570402	0.09137634		

F_AB (XC) 0.18275268

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 1.68162339 -0.92092286 -1.61501369 0.83510850 -0.01920466
EE wself : (coul,XC,self) 0.88454053 -0.04943203 0.00000000
EE woself: (coul,XC) 0.88454053 -0.04943203
Coul comp.: (longr, shortr) 0.950356E+00 -0.658157E-01
Classical Int. (Long,Total) 0.881476E-01 0.302274E-01
RHO_2 Integ comp (TOT,J,XC) 1.89432768 1.98570402 0.09137634
F_AB (XC) 0.18275268

```

Atomic Contributions for neq: 2
 Atom number : 2

```

-----
kinetic energy = 0.59296626
potential energy = -1.02666973
electron repulsion = 0.01285129
---coulomb = 0.31180457
---exch+corr = -0.29895328
---self = 0.00000000
el-own-nuc attraction = -1.02162004
net energy = -0.41580250
interaction energy = -0.03580195
additive energy = -0.43370347
effective energy = -0.45160445
2T+V = 0.15926278
Int rho_2 = 0.04964437
Integ rho_2 J = 0.82215128
Integ rho_2 XC (F_AA) = 0.77250691
SUM-RULE-TEST = 0.90828317 AND SHOULD BE 0.90672558

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.29398736 -0.27305366 -0.27305366 0.23552266 -0.01659729
EE wself : (coul,XC,self) 0.25439166 -0.01886900 0.00000000
EE woself: (coul,XC) 0.25439166 -0.01886900
Coul comp.: (longr, shortr) 0.256641E+00 -0.224982E-02
Classical Int. (Long,Total) 0.473125E-02 0.227170E-02
RHO_2 Integ comp (TOT,J,XC) 0.77775136 0.82215128 0.04439992
F_AB (XC) 0.08879984

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS = 3
# TOTAL NUMBER OF PROBABILITIES = 15
#-----
# Probability n1 n2 n3 ...
# 0.7668810911996232 2 1 1
# 0.0892404850501431 3 1 0
# 0.0892404850501431 3 0 1
# 0.0218915610479210 2 2 0
# 0.0218915610479210 2 0 2
# 0.0087034315047237 4 0 0
# 0.0027118786230455 1 1 2
# 0.0027118786230455 1 2 1
# 0.0000706274467966 1 0 3
# 0.0000706274467966 1 3 0
# 0.000062743332825 0 2 2
# 0.0000018256101396 0 1 3
# 0.0000018256101396 0 3 1

```

```

# 0.0000000444991800 0 0 4
# 0.0000000444991800 0 4 0
#-----
# 1.0034236415920808 <-- SUM, 15 PROBABILITIES > 0.0000000000E+00
# 1.0034236415920808 <--- TOTAL SUM
#-----

```

Average populations and localization indices

```

# <n( 1)> = 2.1971500751
# <n( 2)> = 0.9082722457
# <n( 3)> = 0.9082722457
# <n( 2) n( 1)> = 1.8973974000
# <n( 3) n( 1)> = 1.8973974000
# <n( 3) n( 2)> = 0.7777646567
# <n( 3) n( 2) n( 1)> = 1.5446096969
# delta_( 1 1) = 2.0308130270 % Localization = 92.4294
# delta_( 2 2) = 0.7753037919 % Localization = 85.3603
# delta_( 3 3) = 0.7753037919 % Localization = 85.3603

```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```

# delta_( 2 1) = 0.1827615558
# delta_( 3 1) = 0.1827615558
# delta_( 3 2) = 0.0887389068
# delta_( 3 2 1) = 0.0158936385

```

```

# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3
# -----

```

```

# < S_A^2 > = 0.16391254, < S_AB^2 > = 0.04096640
# rho^1(r1;r1) part = 1.64711697, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.70438422, rho^2(r1,r2;r1,r2) part = -0.94279131
# rho^2(r1,r2;r2,r1) part = -0.77882021, rho^2(r1,r2;r2,r1) part = 0.98375771
# < S_B^2 > = 1.75428327
# rho^1(r1;r1) part = 1.35296901
# rho^2(r1,r2;r1,r2) part = -0.41020514
# rho^2(r1,r2;r2,r1) part = 0.81151940
# -----

```

```

# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3
# -----

```

```

# < S_A^2 > = 0.67783229, < S_AB^2 > = 0.21981969
# rho^1(r1;r1) part = 0.67648450, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.00379558, rho^2(r1,r2;r1,r2) part = -0.67270264
# rho^2(r1,r2;r2,r1) part = 0.00514337, rho^2(r1,r2;r2,r1) part = 0.89252232
# < S_B^2 > = 0.88265695
# rho^1(r1;r1) part = 2.32360148
# rho^2(r1,r2;r1,r2) part = -1.65097112
# rho^2(r1,r2;r2,r1) part = 0.21002658

```

4.13 H-He-H²⁺ LS

Geometries as in the H-He-H calculations.

```

-----
EIGENVECTORS
-----

```

1	2	3	4	5
-1.7745	-0.7108	-0.6074	-0.1802	-0.1331
AG	B1U	AG	AG	B1U

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

1	2	3	4	5
1.9828	0.0094	0.0033	0.0021	0.0021
AG	AG	B1U	B2U	B3U

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.000000000

ONE ELECTRON ENERGY = -5.5261499415

TWO ELECTRON ENERGY = 0.9372315207

NUCLEAR REPULSION ENERGY = 1.8918264891

TOTAL ENERGY = -2.6970919316

ELECTRON-ELECTRON POTENTIAL ENERGY = 0.9372315207

NUCLEUS-ELECTRON POTENTIAL ENERGY = -8.3627712371

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.8918264891

TOTAL POTENTIAL ENERGY = -5.5337132273

TOTAL KINETIC ENERGY = 2.8366212956

VIRIAL RATIO (V/T) = 1.9508114234

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.9956866879E+00	1	-1
-0.6861742770E-01	2	-2
-0.4090585122E-01	3	-3
-0.3236571173E-01	5	-5
-0.3236571173E-01	4	-4

Atomic Contributions for neq: 1
Atom number : 1

kinetic energy	=	2.82044902
potential energy	=	-5.69635042
electron repulsion	=	0.93252948
---coulomb	=	1.98669781
---exch+corr	=	-1.05416833
---self	=	0.00000000
el-own-nuc attraction	=	-6.61613244
net energy	=	-2.86315394
interaction energy	=	-0.02549493
additive energy	=	-2.87590140
effective energy	=	-2.88864887
2T+V	=	-0.05545238
Int rho_2	=	1.97415018
Integ rho_2 J	=	3.94842689
Integ rho_2 XC (F_AA)	=	1.97427670
SUM-RULE-TEST	=	1.98697446 AND SHOULD BE 1.98706489

===== (NN,EN,NE,EE,Inter)	Interaction with atom: 2	===== 0.84081177	-0.85111097	-0.00478240	0.00233413	-0.01274747
EE wself : (coul,XC,self)		0.00483462	-0.00250048	0.00000000		

```

EE woself: (coul,XC)          0.00483462  -0.00250048
Coul comp.: (longr, shorttr)  0.506580E-02 -0.231179E-03
Classical Int. (Long,Total)  -0.143732E-02 -0.102470E-01
RHO_2 Integ comp (TOT,J,XC)   0.00641177   0.01276065   0.00634888
F_AB (XC)                     0.01269775

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)         0.84081177  -0.85111097  -0.00478240   0.00233413  -0.01274747
EE wself : (coul,XC,self)    0.00483462  -0.00250048   0.00000000
EE woself: (coul,XC)         0.00483462  -0.00250048
Coul comp.: (longr, shorttr)  0.506580E-02 -0.231179E-03
Classical Int. (Long,Total)  -0.143732E-02 -0.102470E-01
RHO_2 Integ comp (TOT,J,XC)   0.00641177   0.01276065   0.00634888
F_AB (XC)                     0.01269775

```

```

Atomic Contributions for neq: 2
      Atom number      : 2

```

```

-----
kinetic energy      =      0.00805362
potential energy    =      0.08143451
electron repulsion  =      0.00000117
---coulomb          =              0.00003568
---exch+corr        =             -0.00003451
---self             =              0.00000000
el-own-nuc attraction =     -0.01602764
net energy          =     -0.00797284
interaction energy   =      0.19492196
additive energy     =      0.08948813
effective energy    =      0.18694911
2T+V               =      0.09754176
Int rho_2          =      0.00000148
Integ rho_2 J      =      0.00004124
Integ rho_2 XC (F_AA) =      0.00003976
SUM-RULE-TEST      =      0.00642137  AND SHOULD BE      0.00642186

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter)         0.21020294  -0.00126760  -0.00126760   0.00000168   0.20766942
EE wself : (coul,XC,self)    0.00000811  -0.00000643   0.00000000
EE woself: (coul,XC)         0.00000811  -0.00000643
Coul comp.: (longr, shorttr)  0.767233E-05  0.441363E-06
Classical Int. (Long,Total)  0.207675E+00  0.207676E+00
RHO_2 Integ comp (TOT,J,XC)   0.00000851   0.00004124   0.00003273
F_AB (XC)                     0.00006546

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS          =      3
# TOTAL NUMBER OF PROBABILITIES =      6
#-----
#      Probability          n1    n2    n3 ...
#      0.9870750784660277    2     0     0
#      0.0064117693231979    1     0     1
#      0.0064117693231979    1     1     0
#      0.0000085081111099    0     1     1
#      0.0000007393358618    0     0     2
#      0.0000007393358618    0     2     0
#-----
#      0.9999086038952571 <-- SUM,      6 PROBABILITIES > 0.0000000000E+00
#      0.9999086038952571 <--- TOTAL SUM

```

#-----

Average populations and localization indices

```
# <n( 1)> = 1.9869736956
# <n( 2)> = 0.0064217561
# <n( 3)> = 0.0064217561
# <n( 2) n( 1)> = 0.0064117693
# <n( 3) n( 1)> = 0.0064117693
# <n( 3) n( 2)> = 0.0000085081
# <n( 3) n( 2) n( 1)> = 0.0000000000
# delta_( 1 1) = 1.9739143100 % Localization = 99.3427
# delta_( 2 2) = 0.0000397603 % Localization = 0.6191
# delta_( 3 3) = 0.0000397603 % Localization = 0.6191
```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```
# delta_( 2 1) = 0.0126985147
# delta_( 3 1) = 0.0126985147
# delta_( 3 2) = 0.0000654692
# delta_( 3 2 1) = 0.0001292678
```

```
# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3
```

```
# -----
# < S_A^2 > = 0.00968605, < S_AB^2 > = -0.00961765
# rho^1(r1;r1) part = 1.49029866, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.49353754, rho^2(r1,r2;r1,r2) part = -0.00320588
# rho^2(r1,r2;r2,r1) part = -0.98707508, rho^2(r1,r2;r2,r1) part = -0.00641177
# < S_B^2 > = 0.00961780
# rho^1(r1;r1) part = 0.00963278
# rho^2(r1,r2;r1,r2) part = -0.00000499
# rho^2(r1,r2;r2,r1) part = -0.00000999
```

```
# -----
# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3
```

```
# -----
# < S_A^2 > = 0.00481528, < S_AB^2 > = -0.00481521
# rho^1(r1;r1) part = 0.00481639, rho^1(r1;r1) part = 0.00000000
# rho^2(r1,r2;r1,r2) part = -0.00000037, rho^2(r1,r2;r1,r2) part = -0.00160507
# rho^2(r1,r2;r2,r1) part = -0.00000074, rho^2(r1,r2;r2,r1) part = -0.00321014
# < S_B^2 > = 0.00488368
# rho^1(r1;r1) part = 1.49511506
# rho^2(r1,r2;r1,r2) part = -0.49674379
# rho^2(r1,r2;r2,r1) part = -0.99348759
```

4.14 H-He-H²⁺ LT

Geometries as in the H-He-H calculations.

EIGENVECTORS

1	2	3	4	5
-2.4415	-1.0292	-0.8944	-0.2216	-0.1515
AG	AG	B1U	AG	B1U

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS

	1	2	3	4	5
	0.9987	0.9987	0.0012	0.0012	0.0000
	AG	B1U	AG	B1U	B2G

ENERGY COMPONENTS

WAVEFUNCTION NORMALIZATION = 1.000000000

ONE ELECTRON ENERGY = -4.3879612485

TWO ELECTRON ENERGY = 0.4199226032

NUCLEAR REPULSION ENERGY = 1.8918264891

TOTAL ENERGY = -2.0762121561

ELECTRON-ELECTRON POTENTIAL ENERGY = 0.4199226032

NUCLEUS-ELECTRON POTENTIAL ENERGY = -6.9931707086

NUCLEUS-NUCLEUS POTENTIAL ENERGY = 1.8918264891

TOTAL POTENTIAL ENERGY = -4.6814216163

TOTAL KINETIC ENERGY = 2.6052094601

VIRIAL RATIO (V/T) = 1.7969463446

COEFFICIENT/ OCCUPIED ACTIVE SPIN ORBITALS

0.7068995307E+00	2	-1
-0.7068995307E+00	1	-2
0.1461272377E-01	4	-3
-0.1461272377E-01	3	-4

Atomic Contributions for neq: 1

Atom number : 1

kinetic energy	=	2.02298375		
potential energy	=	-3.81546521		
electron repulsion	=	0.08586120		
---coulomb	=	0.69100727		
---exch+corr	=	-0.60514607		
---self	=	0.00000000		
el-own-nuc attraction	=	-4.07405369		
net energy	=	-1.96520874		
interaction energy	=	0.34545456		
additive energy	=	-1.79248146		
effective energy	=	-1.61975418		
2T+V	=	0.23050229		
Int rho_2	=	0.25528785		
Integ rho_2 J	=	1.20456856		
Integ rho_2 XC (F_AA)	=	0.94928072		
SUM-RULE-TEST	=	1.09753585	AND SHOULD BE	1.09752839

=====
Interaction with atom: 2
=====

(NN,EN,NE,EE,Inter)	0.84081177	-0.46314307	-0.36776002	0.16281860	0.17272728
EE wself : (coul,XC,self)	0.20254683	-0.03972823	0.00000000		
EE woself: (coul,XC)	0.20254683	-0.03972823			
Coul comp.: (longr, shortr)	0.203861E+00	-0.131452E-02			
Classical Int. (Long,Total)	0.214843E+00	0.212456E+00			
RHO_2 Integ comp (TOT,J,XC)	0.42112625	0.49525381	0.07412756		
F_AB (XC)	0.14825513				


```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.84081177 -0.46314307 -0.36776002 0.16281860 0.17272728
EE wself : (coul,XC,self) 0.20254683 -0.03972823 0.00000000
EE woself: (coul,XC) 0.20254683 -0.03972823
Coul comp.: (longr, shorttr) 0.203861E+00 -0.131452E-02
Classical Int. (Long,Total) 0.214843E+00 0.212456E+00
RHO_2 Integ comp (TOT,J,XC) 0.42112625 0.49525381 0.07412756
F_AB (XC) 0.14825513

```

```

Atomic Contributions for neq: 2
  Atom number      : 2

```

```

-----
kinetic energy      = 0.29111868
potential energy    = -0.43298300
electron repulsion  = 0.00103877
---coulomb          = 0.07956495
---exch+corr        = -0.07852617
---self             = 0.00000000
el-own-nuc attraction = -0.53453332
net energy          = -0.24237587
interaction energy   = 0.20102310
additive energy     = -0.14186432
effective energy    = -0.04135277
2T+V                = 0.14925436
Int rho_2           = 0.00367789
Integ rho_2 J       = 0.20362173
Integ rho_2 XC (F_AA) = 0.19994384
SUM-RULE-TEST       = 0.45124976 AND SHOULD BE 0.45124465

```

```

===== Interaction with atom: 3 =====
(NN,EN,NE,EE,Inter) 0.21020294 -0.09414148 -0.09414148 0.00637585 0.02829582
EE wself : (coul,XC,self) 0.04217498 -0.03579913 0.00000000
EE woself: (coul,XC) 0.04217498 -0.03579913
Coul comp.: (longr, shorttr) 0.421759E-01 -0.921499E-06
Classical Int. (Long,Total) 0.640969E-01 0.640950E-01
RHO_2 Integ comp (TOT,J,XC) 0.02644338 0.20362173 0.17717835
F_AB (XC) 0.35435670

```

M-BASINS SPINLESS ELECTRON DISTRIBUTION FUNCTION

```

#-----
# NUMBER OF GROUPS          = 3
# TOTAL NUMBER OF PROBABILITIES = 6
#-----
#   Probability      n1   n2   n3 ...
#   0.4199694019923466    1    0    1
#   0.4199693321705545    1    1    0
#   0.1288679040128165    2    0    0
#   0.0269573471735215    0    1    1
#   0.0021268319614029    0    2    0
#   0.0021268310847750    0    0    2
#-----
# 1.0000176483954170 <-- SUM,      6 PROBABILITIES > 0.0000000000E+00
# 1.0000176483954170 <--- TOTAL SUM
#-----

```

Average populations and localization indices

```

# <n( 1)>          = 1.0976745422
# <n( 2)>          = 0.4511803433
# <n( 3)>          = 0.4511804113
# <n( 2) n( 1)>    = 0.4199693322

```

```

# <n( 3) n( 1)>      =      0.4199694020
# <n( 3) n( 2)>      =      0.0269573472
# <n( 3) n( 2) n( 1)> =      0.0000000000
# delta_( 1 1)      =      0.9471535925 % Localization = 86.2873
# delta_( 2 2)      =      0.1993100382 % Localization = 44.1752
# delta_( 3 3)      =      0.1993101014 % Localization = 44.1753

```

Delocalization indices, Eq. (28) J. Chem. Phys. 126, 094102 (2007)

```

# delta_( 2 1)      =      0.1505422084
# delta_( 3 1)      =      0.1505422182
# delta_( 3 2)      =      0.3532055862
# delta_( 3 2 1)    =      0.0766704847

```

ALLSPINS command has been read in from the input file

```

#
# Fragment A formed by atoms 1
# Fragment B formed by atoms 2 3

```

```

# -----
#          < S_A^2 > =      0.88696825,          < S_AB^2 > =      0.21056312
# rho^1(r1;r1) part =      0.82314629, rho^1(r1;r1) part =      0.00000000
# rho^2(r1,r2;r1,r2) part = -0.06382196, rho^2(r1,r2;r1,r2) part = -0.21056312
# rho^2(r1,r2;r2,r1) part =      0.12764392, rho^2(r1,r2;r2,r1) part =      0.42112625
#          < S_B^2 > =      0.69192761
# rho^1(r1;r1) part =      0.67686697
# rho^2(r1,r2;r1,r2) part = -0.01506064
# rho^2(r1,r2;r2,r1) part =      0.03012127
# -----

```

```

# Fragment A formed by atoms 2
# Fragment B formed by atoms 1 3

```

```

# -----
#          < S_A^2 > =      0.33935296,          < S_AB^2 > =      0.11189241
# rho^1(r1;r1) part =      0.33843349, rho^1(r1;r1) part =      0.00000000
# rho^2(r1,r2;r1,r2) part = -0.00091947, rho^2(r1,r2;r1,r2) part = -0.11189241
# rho^2(r1,r2;r2,r1) part =      0.00183895, rho^2(r1,r2;r2,r1) part =      0.22378481
#          < S_B^2 > =      1.43688433
# rho^1(r1;r1) part =      1.16157977
# rho^2(r1,r2;r1,r2) part = -0.27530455
# rho^2(r1,r2;r2,r1) part =      0.55060911
# -----

```

4.15 H-He-H²⁺ BS

Geometries as in the H-He-H calculations. Real space calculations unnecessary.

```

-----
EIGENVECTORS
-----

```

1	2	3	4	5
-1.7988	-0.7232	-0.7040	-0.2183	-0.1574
A1	A1	B2	A1	B2

```

NATURAL ORBITALS IN ATOMIC ORBITAL BASIS
-----

```

1	2	3	4	5
1.9796	0.0135	0.0028	0.0020	0.0019
A1	A1	B2	B1	A1

```

-----
ENERGY COMPONENTS

```

```

-----
WAVEFUNCTION NORMALIZATION =      1.0000000000

      ONE ELECTRON ENERGY =      -5.5327048134
      TWO ELECTRON ENERGY =       0.9123610411
      NUCLEAR REPULSION ENERGY =    1.9756107487
-----
      TOTAL ENERGY =             -2.6447330237

ELECTRON-ELECTRON POTENTIAL ENERGY =    0.9123610411
NUCLEUS-ELECTRON POTENTIAL ENERGY =   -8.3154471191
NUCLEUS-NUCLEUS POTENTIAL ENERGY =    1.9756107487
-----
      TOTAL POTENTIAL ENERGY =   -5.4274753293
      TOTAL KINETIC ENERGY =     2.7827423057
      VIRIAL RATIO (V/T) =        1.9504052956

```

4.16 H-He-H²⁺ BT

Geometries as in the H-He-H calculations. Real space calculations unnecessary.

```

-----
EIGENVECTORS
-----

```

1	2	3	4	5
-2.4260	-1.1824	-0.8148	-0.2464	-0.1601
A1	A1	B2	A1	B2

```

-----
NATURAL ORBITALS IN ATOMIC ORBITAL BASIS
-----

```

1	2	3	4	5
0.9994	0.9994	0.0004	0.0004	0.0001
A1	A1	B2	B2	A1

```

-----
ENERGY COMPONENTS
-----

```

```

WAVEFUNCTION NORMALIZATION =      1.0000000000

      ONE ELECTRON ENERGY =      -4.4494737458
      TWO ELECTRON ENERGY =       0.4182439289
      NUCLEAR REPULSION ENERGY =    1.9756107487
-----
      TOTAL ENERGY =             -2.0556190683

ELECTRON-ELECTRON POTENTIAL ENERGY =    0.4182439289
NUCLEUS-ELECTRON POTENTIAL ENERGY =   -7.2201679507
NUCLEUS-NUCLEUS POTENTIAL ENERGY =    1.9756107487
-----
      TOTAL POTENTIAL ENERGY =   -4.8263132731
      TOTAL KINETIC ENERGY =     2.7706942048
      VIRIAL RATIO (V/T) =        1.7419148114

```

4.17 Li-Be-Li

CAS[7,4]//6-311+G** calculations. $R_{\text{LiBe}} = 8.00$ au. All energies in au and angles in degrees.

1. Singlet, triplet energies in Li_2

Angle	ESINGLET	ETRIplet
#-----		
180	-14.8640162915	-14.8640089201
170	-14.8640166654	-14.8640088186
160	-14.8640179265	-14.8640084736
150	-14.8640205861	-14.8640077380
140	-14.8640258553	-14.8640062613
130	-14.8640365022	-14.8640032417
120	-14.8640590040	-14.8639968285
115	-14.8640789469	-14.8639911628
110	-14.8641090079	-14.8639826924
100	-14.8642253790	-14.8639507350
95	-14.8643348534	-14.8639216702
90	-14.8645056749	-14.8638777391
85	-14.8647728338	-14.8638115238
80	-14.8651897879	-14.8637122200
75	-14.8658351782	-14.8635641753
70	-14.8668172157	-14.8633442042
65	-14.8682675873	-14.8630154128
60	-14.8703092363	-14.8625118139
50	-14.8760687111	-14.8603078125
40	-14.8800768745	-14.8528858297
30	-14.8632556745	-14.8247078821
20	-14.7693660110	-14.7275683186
10	-14.2257515608	-14.1595838563

2. Singlet, triplet energies in Li-Be-Li

Angle	ESINGLET	ETRIplet
#-----		
180	-29.4355480285	-29.4350697655
170	-29.4355376664	-29.4350712209
160	-29.4355066397	-29.4350759487
150	-29.4354550889	-29.4350850004
140	-29.4353831903	-29.4351000235
130	-29.4352913819	-29.4351230707
120	-29.4351816115	-29.4351561443
115	-29.4351219943	-29.4351767859
110	-29.4350619088	-29.4351999971
105	-29.4350053140	-29.4352252089
100	-29.4349593395	-29.4352512476
95	-29.4349363814	-29.4352760258
90	-29.4349575404	-29.4352961360
85	-29.4350578987	-29.4353063276
80	-29.4352940327	-29.4352987915
75	-29.4357532099	-29.4352619843
70	-29.4365608029	-29.4351782397
60	-29.4398572061	-29.4347285476

3. Densities at the bond critical point ρ_{bcP} in the singlet and triplet Li-Be-Li

Angle	rhob s	rhob t
#-----		
180	0.238910258E-02	0.230549032E-02

170	0.238719165E-02	0.230530755E-02
160	0.238149998E-02	0.230487429E-02
150	0.237233652E-02	0.230450644E-02
140	0.236008275E-02	0.230462035E-02
130	0.234524516E-02	0.230563773E-02
120	0.232834751E-02	0.230784711E-02
115	0.231930863E-02	0.230944821E-02
110	0.231011185E-02	0.231138336E-02
105	0.230100513E-02	0.231365771E-02
100	0.229237808E-02	0.231626382E-02
95	0.228492857E-02	0.231920130E-02
90	0.227973264E-02	0.232244225E-02
85	0.227857929E-02	0.232593967E-02
80	0.228437179E-02	0.232960161E-02
75	0.230181108E-02	0.233329603E-02
70	0.233864717E-02	0.233692547E-02
60	0.252963063E-02	0.234534634E-02

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