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

Electronic Supplementary Information.

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Contents

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's[2] 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 energy[3] described in the following equation,

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

wherein $E_{\mathrm{self}}^{\mathrm{A}}$ and $E_{\mathrm{int}}^{\mathrm{AB}}$ 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 $V_{\mathrm{ne}}^{\mathrm{AB}}$ and $V_{\mathrm{ee}}^{\mathrm{AB}}$ 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 as[3]

$$E_{\mathrm{int}}^{\mathrm{AB}} = V_{\mathrm{cl}}^{\mathrm{AB}} + V_{\mathrm{xc}}^{\mathrm{AB}} = E_{\mathrm{ion}}^{\mathrm{AB}} + E_{\mathrm{cov}}^{\mathrm{AB}}. \tag{2}$$

Usually binding is measured relative to appropriate reference for the quantum fragments A, with $E^{A,0}$ energies. Then $E_{self}^{A} - E^{A,0} = E_{def}^{A}$ 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 Ω_1, Ω_2, …, Ω_m ($\Omega_1 \cup \Omega_2 \cup \cdots \cup \Omega_m = \mathcal{R}^3$), an EDF is the distribution function formed by all the probabilities $p(n_1, n_2, \ldots, n_m)$ of finding exactly n_1 electrons in Ω_1, n_2 electrons in Ω_2, …, and n_m electrons in Ω_m, $\{n_p\}$ being integers ($n_i \in \mathcal{N}$) satisfying $n_1 + n_2 + \cdots + n_m = N$. 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, $\hat{N}_{\Omega_i}$. This means that the average number of electrons in Ω_i is not an eigenvalue of $\hat{N}_{\Omega_i}$, 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 $p(n_1, n_2, \cdots, n_m)$, one needs $\Psi(1, \ldots, N)$, Ψ being the complete wave function,

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

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, $\cdots$, 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 was 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 $S(n_1, n_2, \ldots, n_m) \equiv S(\{n_p\})$, or simply $(n_1, n_2, \ldots, n_m) \equiv \{n_p\}$, we label the resonance structure having n_1 electrons in Ω_1, n_2 electrons in Ω_2, …, and n_m electrons in Ω_m. If electrons are spin-seggregated, then we come to spin-resolved EDFs, and a set of probabilities $p(n_1^\alpha, n_1^\beta, n_2^\alpha, n_2^\beta, \ldots, n_m^\alpha, n_m^\beta)$ which gives extremely fine-grained information about how electrons and their spins distribute.[6]

The computation of $p(n_1, n_2, \ldots, n_m)$ 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

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

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

$$\delta^{ij} = -2\mathrm{cov}(i,j) = -2\left[\langle n_i n_j\rangle - \langle n_i\rangle\langle n_j\rangle\right] = \tag{5}$$

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

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

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,

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

The localization index is given by

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

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:

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

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 RSRSs: $(2,0)$, $(1,1)$, $(0,2)$, 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,

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

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

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

where $\rho(\boldsymbol{r}_1)$ is the electron density at point $\boldsymbol{r}_1$ and $\rho^2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2)$ 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 $\hat{p}_{ij}^{\sigma}$ 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 $\langle \Psi | \hat{O} | \Psi \rangle = -\frac{1}{2}\int \rho^2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_2, \boldsymbol{r}_1)\, d\boldsymbol{r}_1 d\boldsymbol{r}_2$.

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

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

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,

$$\begin{aligned} \langle \hat{S}_A^2 \rangle &= \frac{3}{4}\int_A \rho(\boldsymbol{r}_1) d\boldsymbol{r}_1 + \int_A \int_A F(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2, && (14) \\ \langle \hat{\boldsymbol{S}}_A \cdot \boldsymbol{S}_B \rangle &= \int_A \int_B F(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2, \qquad \text{where} && (15) \\ F(\boldsymbol{r}_1, \boldsymbol{r}_2) &= -\frac{1}{4}\rho^2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2) - \frac{1}{2}\rho^2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_2, \boldsymbol{r}_1). && (16) \end{aligned}$$

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),

$$\begin{aligned} \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2) &= \rho(\boldsymbol{r}_1; \boldsymbol{r}_1)\rho(\boldsymbol{r}_2; \boldsymbol{r}_2) - \frac{1}{2}\rho(\boldsymbol{r}_1; \boldsymbol{r}_2)\rho(\boldsymbol{r}_2; \boldsymbol{r}_1), \qquad \text{and} && (17) \\ \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_2, \boldsymbol{r}_1) &= \rho(\boldsymbol{r}_1; \boldsymbol{r}_2)\rho(\boldsymbol{r}_2; \boldsymbol{r}_1) - \frac{1}{2}\rho(\boldsymbol{r}_1; \boldsymbol{r}_1)\rho(\boldsymbol{r}_2; \boldsymbol{r}_2), && (18) \end{aligned}$$

so that

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

Then,

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

The localization index inside A is given by

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

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

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

where $N_A = \int \rho(\boldsymbol{r}) d\boldsymbol{r}$ 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

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

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

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

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

$$\begin{aligned}
\Psi_{S,cov} &= \frac{1}{\sqrt{2(1+S^2)}}(a(1)b(2)+b(1)a(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow), && (25)\\
\Psi_{S,ion} &= \frac{1}{\sqrt{2(1+S^2)}}(a(1)a(2)+b(1)b(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow). && (26)\\
\Psi_{T} &= \frac{1}{\sqrt{2(1-S^2)}}(a(1)b(2)-b(1)a(2))\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow). && (27)
\end{aligned}$$

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

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

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

$$\Psi_{gg} = \Psi_{\text{HF}} = |g\bar{g}|,\ \Psi_{uu} = |u\bar{u}|. \tag{29}$$

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

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

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

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

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,

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

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 $|g\bar{g}|$ and $|u\bar{u}|$ determinants differ in two spinorbitals, so only the 2RDM has coupling terms,

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

Similarly, for the triplet

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

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

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

which can be written as $2\varphi_a(\boldsymbol{r}_1)\varphi_b(\boldsymbol{r}_1)\varphi_a(\boldsymbol{r}_2)\varphi_b(\boldsymbol{r}_2)$. 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

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

and given that the orthogonality of φ_a and φ_b also implies that $\int_\Omega \varphi_a(\boldsymbol{r})\varphi_b(\boldsymbol{r}) = 0$, 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 structure[14]:

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

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

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:

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

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-Chebychev 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                      COORDINATES (BOHR)
          CHARGE          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                      COORDINATES (BOHR)
          CHARGE         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, shortr)  -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, shortr)  -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, shortr)   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                      COORDINATES (BOHR)
           CHARGE         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, shortr)   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, shortr)   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                      COORDINATES (BOHR)
           CHARGE         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, shortr)   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 =       1.0000000000

               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

===================  Interaction with atom:   2  =================================================
(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 =       1.0000000000

               ONE ELECTRON ENERGY =      -1.4342355455
               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

===================  Interaction with atom:   2  =================================================
(NN,EN,NE,EE,Inter)              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-H^{2+} 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, shortr)   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, shortr)   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, shortr)   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-H^{2+} 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-H^{2+} 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-H^{2+} 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 =       1.0000000000

                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

 ===================  Interaction with atom:   2  =================================================
 (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
 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
#     0.0000062743332825      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-H^{2+} 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 =       1.0000000000

               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

 ===================  Interaction with atom:   2  ==================================================
 (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, shortr)   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, shortr)   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, shortr)   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-H^{2+} 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 =       1.0000000000

                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, 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

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, shortr)   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-H^{2+} 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-H^{2+} 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. $R_{\mathrm{LiBe}} = 8.00$ 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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