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RESEARCH ARTICLE

Local Spin from Strongly Orthogonal Geminal Wavefunctions

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Covalent bond dissociation is examined by three geminal based theories. One approach (Antisymmetrized Product of Strongly Orthogonal Geminals, APSG) assumes purely singlet geminals while two others operate with mixtures of singlets and triplets (c.f. Restricted-Unrestricted Strongly orthogonal Singlet-type Geminals, RUSSG). The RUSSG is the wavefunction in the second method. It is spin contaminated. The spin contamination of RUSSG is projected out in a spin purification step in the third method.

Description of local (i.e. atomic) spin by geminal based theories is examined. Prototype systems showing the deficiency of singlet coupling are taken as test cases. We find that the local spin of equilibrium structures is correctly described by purely singlet geminals. Triplet geminals are shown to be essential for the description of local spin when dissociating multiple bonds, or switching between two Lewis structures of the same molecule.

Keywords: geminal, strong orthogonality, singlet coupling, spin unrestricted, local spin

1. Introduction

Inadequacy of the single determinant approximation of the molecular electronic wavefunction for describing covalent bond dissociation or transition metal compounds has long been a challenge for quantum chemistry. Qualitative defects of the Hartree-Fock (HF) method can be cured by a theory initiated in the 1920's by the seminal paper of Heitler and London[1]: Valence Bond (VB). Though VB fits a chemist's notion of molecules better than HF, it became computationally cumbersome compared to molecular orbital (MO) theory and got overshadowed around

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the 1960's. Progress along the VB line has been constant though[2, 3, 4, 5, 6]. Development of valence bond inspired methods has got more active recently, with applications aided by program packages, see e.g. Ref.[7].

Geminal based wavefunctions represent a type of VB, where a single resonance structure is assumed. The elementary building block in geminal theories is a two-electron function, ψ expanded in terms of one-electron spin-orbitals, φ_u and φ_v as

$$\psi_i^+ = \sum_{u<v} C_{uv}^i \varphi_u^+ \varphi_v^+$$

adopting the Longuet-Higgins notation for creation operators. The single VB structure of geminal theories is expressed as the antisymmetrized product

$$\Psi = \prod_{i=1}^{N/2} \psi_i^+ |\text{vac}\rangle, \quad (1)$$

for a molecule containing N electrons. Terminology 'perfect pairing' (PP) is also used to refer to a single resonance structure wavefunction, Eq.(1).

There are numerous alternatives behind the general form of Eq.(1), the question of orthogonality making an essential distinction. In analogy with orthogonality of one-electron orbitals, one may require the relation

$$\langle \psi_i | \psi_j \rangle = 0, \quad i \neq j \quad (2)$$

for geminals, addressed as 'weak orthogonality'. A condition called 'strong orthogonality' proved extremely useful in practice, given by

$$\int d\mathbf{x}_1 \psi_i(\mathbf{x}_1, \mathbf{x}_2) \psi_j(\mathbf{x}_1, \mathbf{x}_2) = 0, \quad i \neq j. \quad (3)$$

Restriction on geminals is obviously more severe by Eq.(3) than by Eq.(2). The benefit of requirement Eq.(3) lies with the fact that matrix elements of the Hamiltonian are considerably easier to calculate with strongly orthogonal geminals than with weakly orthogonal ones. Group function theory allows a generalization of the concept of strong orthogonality, investigated originally by Wilson[8] and addressed by Cassam-Chennai[9, 10] more recently.

Current, active research directions in the field of strongly orthogonal geminals involve convergence acceleration of orbital optimization[11], excited state calculation based on the generalized equation of motion[12], as well as coupled cluster inspired

treatments[13, 14, 15]. An overview of geminal based perturbative techniques for describing electron correlation was given recently[16].

Besides orthogonality, geminal spin is another major attribute of geminal based wavefunctions. A wavefunction of Eq.(1) composed of pure singlet ψ_i 's is called singlet coupled. The Antisymmetrized Product of Strongly Orthogonal Geminals (APSG)[17] as well as the Restricted Strongly orthogonal Singlet-type Geminals (RSSG)[18] represent examples of this sort. The Generalized Valence Bond (GVB) wavefunction[19] also belongs to this category.

It has long been understood that multiple bond dissociation described by solely singlet geminals is qualitatively incorrect[20]. When dissociating multiple bonds, neglect of triplet electron pairs results an incorrect spin state of the dissociated fragments. Assuming orbitals localized on fragments, local spin can be easily evaluated in the limit of dissociation. Considering e.g. the infinite stretch of both OH bonds in the water molecule, a GVB approach results a spin-contaminated state for atom O, characterized by $S(S+1)=3/2$, instead of the correct value $S(S+1)=2$, i.e. a triplet. Incorrect spin of the fragment is a direct consequence of the simplification introduced in spin coupling. To correct for this, spin impure geminals, i.e. mixtures of singlet and triplet have been adopted[21, 22].

It is not only multiple bond dissociation, where the weakness of singlet coupling shows up. The rectangular to square distortion of H_4 , a model introduced by Jankowski and Paldus[23] is another problematic case. Singlet coupling here produces a cusp on the energy curve at the square arrangement. The flaw can again be attributed to an insufficient description of spin couplings. Alternatively, one can regard the problem as an indication for the necessity of two singlet coupled VB structures.

The aim of the present study is to assess the error of singlet coupling in geminal wavefunctions in a quantitative manner, by computing atomic spin. While atomic spin is easy to grasp at infinite separation, it is not straightforward to define this quantity when atoms interact in a molecule. Among several possibilities, a definition given by Mayer and coworkers is adopted here[24]. Besides quantifying the defect of the singlet coupled geminal model in estimating local spin, we wish to demonstrate that allowing geminals to become (partly) triplet represents a solution while staying with PP. Singlet-triplet mixed geminals induce spin contamination in the overall wavefunction of Eq.(1). The effect of a final spin-purification is examined, along the lines suggested by one of us[25]. The approximate spin-purification

scheme introduced in Ref.[26] is not investigated presently.

We believe that this study on local spin contributes to the understanding of the capabilities of geminal based models. Apart from being interesting on its own right, limitations of the geminal model are important from the point of view of correlation corrections based upon such a model. Whenever qualitative breakdown of a reference function occurs, one may expect the influence to appear in the construction build upon. In fact, indications of such an effect has been observed in a linearized coupled-cluster study based on the APSG wavefunction[27].

In what follows, a brief summary is given of the geminal based approaches applied. After a short account of the computation of atomic spin, examples are presented and discussed in the final section. A case study showing the connection between the geminal spin coupling and fragment spin is given in the Appendix.

2. Variants for strongly orthogonal geminals

2.1. Singlet coupling

Among the models examined, APSG is the simplest, where geminals are assumed singlet. Introducing indices m, n for spatial orbitals and α, β for spin, a geminal is written as

$$\psi_i^+ = \frac{1}{2} \sum_{mn} C_{mn}^i \left(\varphi_{m\alpha}^+ \varphi_{n\beta}^+ + \varphi_{n\alpha}^+ \varphi_{m\beta}^+ \right), \quad (4)$$

with $C_{mn}^i = C_{nm}^i$ and $\sum_{mn} (C_{mn}^i)^2 = 1$ reflecting normalization of geminal i .

The APSG wavefunction is expressed according to Eq.(1), with geminals of Eq.(4). The model is fully variational, meaning that geminal coefficients C_{mn} as well as expansion coefficients of orbitals φ_m are determined by energy minimization[17]. The APSG wavefunction is also extensive, as a consequence of its exponential form[28, 29].

Due to the requirement of strong orthogonality, an orbital φ_m can appear in just one geminal[30]. The variational energy minimization is usually achieved by the orbital variation that maximizes the energy coupling between the orbital pairs of the same geminal, leading to spatial orbital localization. Optimal orbitals φ_m are typically localized in the region of space where one would expect the corresponding electron pair to reside.

The GVB wavefunction represents a variant of APSG with two orbitals assigned

to each valence geminal. An APSG model where the number of orbitals contributing to a geminal is also optimized was termed RSSG[18]. Presently we stick with the APSG terminology for this wavefunction.

2.2. Beyond singlet coupling

One way to introduce triplet component in a geminal is to consider unrestricted orbitals. This leads to the USSG model, 'U' referring to unrestricted[18]. Unrestricted perfect pairing is an alternative designation of essentially the same model[22].

Presently we will be considering restricted orbitals and allow triplet components to enter via the geminal coefficient matrix. In this, restricted-unrestricted (RUSSG) formulation[21] geminals are written as

$$\psi_i^+ = \sigma_i {}^1\psi_i^+ + \tau_i {}^3\psi_i^+ \quad (5)$$

where ${}^1\psi_i^+$ stands for the normalized singlet component

$${}^1\psi_i^+ = \frac{1}{2} \sum_{mn} {}^1C_{mn}^i \left(\varphi_{m\alpha}^+ \varphi_{n\beta}^+ + \varphi_{n\alpha}^+ \varphi_{m\beta}^+ \right),$$

and ${}^3\psi_i^+$ constitutes the normalized, $s_z = 0$ triplet component

$${}^3\psi_i^+ = \frac{1}{2} \sum_{mn} {}^3C_{mn}^i \left(\varphi_{m\alpha}^+ \varphi_{n\beta}^+ - \varphi_{n\alpha}^+ \varphi_{m\beta}^+ \right),$$

with ${}^3C_{mn}^i = -{}^3C_{nm}^i$ and $\sum_{mn} ({}^3C_{mn}^i)^2 = 1$. Condition $\sigma_i^2 + \tau_i^2 = 1$ sets geminal i normalized.

Writing the geminal of Eq.(5) in the compact form

$$\psi_i^+ = \sum_{mn} C_{mn}^i \varphi_{m\alpha}^+ \varphi_{n\beta}^+, \quad (6)$$

one finds that the symmetric/antisymmetric part of the coefficient matrix is related to the singlet/triplet component according to

$$C_{mn}^i = \sigma_i {}^1C_{mn}^i + \tau_i {}^3C_{mn}^i.$$

Geminal coefficients C_{mn}^i , orbitals φ_m and number of orbitals belonging to geminal Eq.(6) are determined in a variational manner. Size-consistency of RUSSG was proven and demonstrated numerically in Ref.[21]. In the context of GVB, UAP is a related model (standing for Unrestricted orbitals in Active Pairs), assuming two

active orbitals per geminal[31]. Orbitals optimized for RUSSG tend to be similar to APSG orbitals if the triplet component of the geminal is small. As the triplet component of a geminal gets large, orbital delocalization may be observed, c.f. the example of H_4 in Section 4.

Due to strong orthogonality, spin-impurity of electron pairs in RUSSG is localized on the geminal. This gives rise to a spin-contamination of the total wavefunction which can be purified efficiently[25]. Writing the total wavefunction as

$$\Psi_{\text{RUSSG}} = \sum_{S=0} \sigma_S {}^{2S+1}\Psi$$

with $\hat{S}^2 {}^{2S+1}\Psi = S(S+1) {}^{2S+1}\Psi$, the goal of spin-purification for an overall singlet state is to remove $S > 0$ terms. The spin-projected (SP) RUSSG wavefunction is given by term $S = 0$ (supposed to be normalized):

$$\Psi_{\text{SP-RUSSG}} = {}^1\Psi .$$

Spin-purification of Ψ_{RUSSG} proceeds in two-steps. First a set of functions are generated by the repeated action of \hat{S}^2 on Ψ_{RUSSG} . Vectors

$$\left(\hat{S}^2\right)^n \Psi_{\text{RUSSG}} = \sum_{S=0} \sigma_S (S(S+1))^n {}^{2S+1}\Psi , \quad n = 0, \dots \quad (7)$$

can be thought of forming a Krylov space. In the second step the Hamiltonian eigenvalue problem is solved in the Krylov space. The lowest root does in fact generate spin-pure wavefunction, since (i) the spectrum of \hat{S}^2 is nondegenerate in this space and (ii) matrices of \hat{S}^2 and \hat{H} written in the Krylov space commute[25]. We note here that the energy of spin-purified $\Psi_{\text{SP-RUSSG}}$ wavefunction can be improved further by variation of geminal coefficients C_{mn}^i (which are kept frozen in the spin-purification procedure). This is tested in one case in Section 4, where it is labeled 'SP-RUSSG, opt'.

Efficient realization of spin-purification is facilitated by the geminal picture. Action of \hat{S}^2 on Ψ_{RUSSG} generates $s_z = \pm 1$ spin-polarized triplets, having the form

$$\begin{aligned} {}^3_1\psi_i^+ &= \frac{1}{\sqrt{2}} \sum_{mn} {}^3C_{mn}^i \varphi_{m\alpha}^+ \varphi_{n\alpha}^+ , \\ {}^3_{-1}\psi_i^+ &= \frac{1}{\sqrt{2}} \sum_{mn} {}^3C_{mn}^i \varphi_{m\beta}^+ \varphi_{n\beta}^+ . \end{aligned}$$

Antisymmetrized product of ${}^1\psi_i$, ${}^3_0\psi_i$, ${}^3_1\psi_i$ and ${}^3_{-1}\psi_i$ are used to compose basis

vectors

$$B(n_+, n_0) = \sum_{\hat{P} \in S_{N/2}} \prod_{l=P_{n_0+2n_++1}}^{P_{N/2}} {}^1\psi_l^+ \prod_{k=P_{n_0+n_++1}}^{P_{n_0+2n_++1}} {}^3_{-1}\psi_k^+ \prod_{j=P_{n_0+1}}^{P_{n_0+n_++1}} {}^3_1\psi_j^+ \prod_{i=P_1}^{P_{n_0}} {}^3_0\psi_i^+ |\text{vac}\rangle \quad (8)$$

categorized according to the number of $s_z = 1$ triplets, n_+ and the number of $s_z = 0$ triplets, n_0 . (Due to seeking total $S_z = 0$, the number of $s_z = -1$ triplets is also n_+ .) Calculation of operator matrix elements among vectors B is computationally inexpensive, based on the results of Ref.[25]. For this reason, vectors $B(n_+, n_0)$ are used to represent the Krylov vectors of Eq.(7). The generalization of this procedure to the open-shell case is given in Ref.[25].

Performance of the SP-RUSSG wavefunction has not been explored in detail, though initial tests were encouraging. The present study takes a small step in this direction, giving a characterization mainly from the local spin point of view.

3. Local spin

Local spin is a spin like quantity assigned to atoms and pairs of atoms in a molecule, giving information about magnetic properties and electronic structure[32, 33, 34]. The straightforward approach for determining such quantity is to partition operator S^2 to atomic and diatomic contributions and calculate local spin as an expectation value of the appropriate term. In this definition the diatomic part of the local spin would be proportional to the bond order[35], meaning that electron pairs coupled singlet in covalent bonds have nonzero contribution to the local spin. This contradicts the physical concept that magnetic properties are determined by open-shell or "actually free" electrons[36, 37]. For this reason Mayer introduced an alternative definition for single determinant wavefunction[35], based on the decomposition of the expectation value of \hat{S}^2 , instead of the operator itself. The advantage of this definition is that every term depends on the spin density matrix ($\mathbf{P}^s = \mathbf{P}^\alpha - \mathbf{P}^\beta$), and becomes zero for singlet coupled electrons. Since the first formulation, the way of partitioning has evolved and generalization for multi-determinant wavefunction has been developed[38, 39, 40, 41, 42]. Final version of the theory was settled by Ramos-Cordoba *et al.* [24], who also studied basis set dependence and compared the benefits of decomposing in Hilbert-space or in 3D-space[43].

In the present study atomic and diatomic terms of the local spin are computed

according to [24]:

$$\begin{aligned} \langle \hat{S}^2 \rangle_A &= \frac{3}{4} \sum_{\mu \in A} [2\mathbf{D}\mathbf{S} - (\mathbf{D}\mathbf{S})^2]_{\mu\mu} + \frac{1}{4} (p_A^s)^2 - \frac{1}{4} \sum_{\mu, \nu \in A} (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu} \\ &\quad + \frac{1}{2} \sum_{\mu, \nu \in A} \sum_{\tau, \rho} [\Lambda_{\mu\nu\rho\tau} - \Lambda_{\mu\nu\tau\rho}] S_{\rho\mu} S_{\tau\nu} \end{aligned} \quad (9)$$

$$\begin{aligned} \langle \hat{S}^2 \rangle_{AB} &= \frac{1}{4} p_A^s p_B^s - \frac{1}{4} \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu} \\ &\quad + \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\tau, \rho} [\Lambda_{\mu\nu\rho\tau} - \Lambda_{\mu\nu\tau\rho}] S_{\rho\mu} S_{\tau\nu}, \end{aligned} \quad (10)$$

where A, B refer to atoms, \mathbf{S} is the overlap matrix, $\mathbf{D} = \mathbf{P}^\alpha + \mathbf{P}^\beta$ is the spin-less density matrix (DM), and p_A^s is the gross spin population:

$$p_A^s = \sum_{\mu \in A} (\mathbf{P}^s \mathbf{S})_{\mu\mu}.$$

The spin-less cumulant, Λ can be expressed as:

$$\Lambda_{\mu\nu\rho\tau} = \Gamma_{\mu\nu\rho\tau} - D_{\mu\rho} D_{\nu\tau} + \sum_{\sigma} P_{\mu\tau}^{\sigma} P_{\nu\rho}^{\sigma},$$

where $\Gamma (= \sum_{\sigma, \sigma'} \Gamma^{\sigma\sigma'})$ is the spin-less two-particle DM and σ, σ' label spin indices. In the above, μ and ν refer to atomic orbitals, which implies a Mulliken-like partitioning[44] of $\langle \hat{S}^2 \rangle$.

Due to the geminal structure the one-particle DM has a block diagonal form for APSG and RUSSG, P_{mn}^{σ} being equal to zero if m and n belong to different geminals. The two-particle $\Gamma_{mnl s}^{\sigma\sigma}$ is zero too if l and s or m and n belong to the same geminal. Otherwise:

$$\Gamma_{mnl s}^{\sigma\sigma} = D_{ml}^{\sigma} D_{ns}^{\sigma} - D_{ms}^{\sigma} D_{nl}^{\sigma}.$$

The different spin term $\Gamma^{\sigma\sigma'}$ ($\sigma \neq \sigma'$) can be written in the following form:

$$\Gamma_{mnl s}^{\sigma\sigma'} = D_{ml}^{\sigma} D_{ns}^{\sigma'} + \Lambda_{mnl s}^{\sigma\sigma'}$$

where $\Lambda_{mnl s}^{\sigma\sigma'}$ is nonzero only if all of its indices belong to the same geminal.

When calculating DM's with SP-RUSSG the geminal structure was not exploited. Generation of the necessary quantities was performed based on the expansion of the wavefunction in terms of vectors B of Eq.(8).

4. Assessment of local spin by strongly orthogonal geminals

In this section we present the local spin property of APSG, RUSSG and SP-RUSSG compared to FCI. Local spin is obviously a non-measurable quantity, apart from the limit of fully dissociated atoms. By computing the spin of an atom within a molecule and comparing it to the corresponding exact (i.e. FCI) value, we imply that local spin is a property, which – though non-measurable – serves for characterization of the wavefunction.

To compute the local spin of Eq.(9) one needs overlap matrices, the one-particle DM and the cumulant (i.e. two-particle DM). Density matrices with APSG and RUSSG were generated by the modified version of Q-Chem [45]. Density matrices with SP-RUSSG were obtained by a direct Full Configuration Interaction (FCI) code. Due to the large memory and computer time requirement of FCI, only small test systems were affordable. All reported FCI energies assume cores frozen.

4.1. *Water symmetric dissociation*

While single bond dissociation is accurately described by established geminal methods, dissociation of multiple bonds may be problematic. To describe e.g. the symmetric dissociation of water four active electrons are needed. Geminal type methods can be unsatisfactory because of artificial separation of the four electrons into two pairs. The potential curve in Fig.1, computed with 6-31G** basis, does not show any qualitative failure for APSG, RUSSG or SP-RUSSG. When looking at error curves computed with FCI (c.f. panel (b) of Fig.1), one sees that geminal methods produce an error on the scale of a few tens of millihartree in the 1-3 Å in the bond length interval. Curves of APSG, RUSSG and SP-RUSSG run together until about 2 Å, where the spin contamination appears in the RUSSG wavefunction. From this point the energy of RUSSG and SP-RUSSG gets markedly deeper than APSG causing larger nonparallelism error.

Local spin curves cast a different light on the case. When forming a molecule of atoms, the high multiplicity of the free atom typically drops to a low value at molecular equilibrium. This is apparent on the FCI curves in panel (a) of Figs. 2 and 3. Local spin of hydrogen and oxygen behave in a completely different manner: $\langle S^2 \rangle_H$ with geminal methods estimate the FCI result well, which does not hold for $\langle S^2 \rangle_O$. Oxygen local spin is the worst by APSG, giving a large error at the dissociation limit. This qualitative error is eliminated both by RUSSG and SP-

RUSSG. Finer details are revealed by the difference curves in panels (b). The largest errors can be found in the 1.5-3 Å bond distance range. At about 2 Å one can see a negative peak for oxygen with RUSSG. At this geometry the spin contamination is not significant yet, the error can be attributed to perfect pairing. Once spin contamination appears the (signed) error of RUSSG starts to increase forming a positive peak about 2.5 Å. A similar positive peak is apparent on the hydrogen curve (Fig. 3). In the dissociation limit local spin by RUSSG tends to the correct value. Spin purification diminishes the error of RUSSG by shaving off the positive peaks from the difference curves.

4.2. Nitrogen molecule dissociation

In the complete active space approach nitrogen dissociation has to include six active electrons. Geminal methods assign the six electrons to three bonds, which may prevent correct description of the quartet state of free nitrogen atoms. The total energy curve, computed with 6-31G basis, move together for APSG, RUSSG and SP-RUSSG (see Fig. 4) until spin contamination appears around 2 Å. Beyond 2 Å RUSSG and SP-RUSSG produce significantly deeper energies increasing the nonparallelism error.

Similarly to the water example, APSG gives an erroneous local spin near to dissociation, while RUSSG is qualitatively correct, c.f. Fig. 5. There is again a small peak on the local spin difference curve around 2 Å, which is diminished by spin purification. It is interesting to note here that a small (about 10 millihartree) hump appears in the same distance regime on the total energy curve of RUSSG, which is much flattened by SP-RUSSG.

4.3. H_4 system

The last example is the H_4 system, computed with 6-31G** basis. The four hydrogens are confined to a circle and the initial drawn rectangle is gradually distorted to a square. Change of geometry is characterized by the (H-X-H) angle where X refers to the center of mass. The challenge of this system is the simultaneous breaking and formation of covalent bonds.

The energy curve of APSG shows a characteristic cusp at the square geometry, formed by the crossing of two distinct solutions: one with orbitals localized on horizontally aligned hydrogen molecules, the other corresponding to vertically

aligned H_2 systems. The two resonance structures are degenerate at exactly 90° . As apparent in Fig. 6, no cusp appears on the RUSSG and SP-RUSSG curves which can mainly be attributed to orbital delocalization[25]. The curve labeled "APSG deloc" underlines this statement, showing a stationary solution of the APSG equations, giving delocalized orbitals and higher energy than APSG, but no cusp at 90° . Triplet component of the geminals appear somewhat below 88° , causing a step on the SP-RUSSG curve but not on RUSSG, see the inset in panel (b) of Fig. 6. Discontinuity on the SP-RUSSG curve is not surprising, bearing in mind that the underlying procedure is essentially projection after variation. Performing (partial) variation after projection removes the discontinuity, c.f. curve 'SP-RUSSG, opt'.

The dissociation like process is manifested by an increase in the local spin of hydrogen as can be seen in Fig. 7. Bonds are restructured but not completely broken in this example, hence the atomic spin of H is not raised up to the free atomic value at square geometry. While APSG with localized orbitals can not reflect the increase of local spin, RUSSG corrects this behavior abruptly once spin-contamination appears. Appearance of triplet components of geminals is accompanied by orbital delocalization, occurring just below 88° for RUSSG. Spin-purification has a decreasing effect on local spin, setting the error larger than RUSSG near to square geometry. Coefficient optimization of SP-RUSSG improves at square geometry and removes the step near to 88° . There occurs however a switch between localized and delocalized solutions for 'SP-RUSSG, opt' also. This is responsible for the smaller step on the local spin curve just above 86° . Interestingly, when taking the solution of APSG with delocalized orbitals, one gets a local spin curve parallel with FCI and the best values at smaller angles.

Overlap values with the FCI vector, displayed in Fig. 8, give another look on the quality of the wavefunction and largely lead to conclusion similar to the above. Overlap of APSG with localized orbitals decreases approaching the square geometry. Allowing spin-contamination of geminals gives worse results, c.f. RUSSG. It is spin projection which improves the overlap at larger angles, as apparent on the SP-RUSSG curve. Coefficient optimization, when in effect, pushes the overlap very close to 1. The overlap of APSG with delocalized orbitals here also gives a flat curve impressively close to 1. Notably, APSG with localized orbitals has smaller overlap with FCI, than the higher energy, delocalized solution.

5. Conclusion

Local spin has been computed to examine the ability of geminal models to describe the coupling of high atomic spin to an overall low value.

Multiple bond dissociation represents an example where such a question is of high relevance. While the singlet coupled geminal model shows qualitative failure in this respect, singlet-triplet mixture of geminals brings a considerable improvement in the regime of moderately stretched bonds and set the picture right at infinite dissociation. Parallelity of the energy with FCI is at the same time worsened by abandoning singlet-coupling.

Describing the "resonance" of two Lewis structures is a more challenging example, where the nature of orbitals has been found an essential ingredient in agreement with a related study[46]. Singlet coupled geminals are completely incapable of reflecting the increase of local spin in the switching region. This gets corrected if allowing triplet components of geminals to build up. The correction however appears abruptly on local spin curves. Spin-purification followed by variation has been found superior, but still failing to give a smooth transition from low local spin to a high value.

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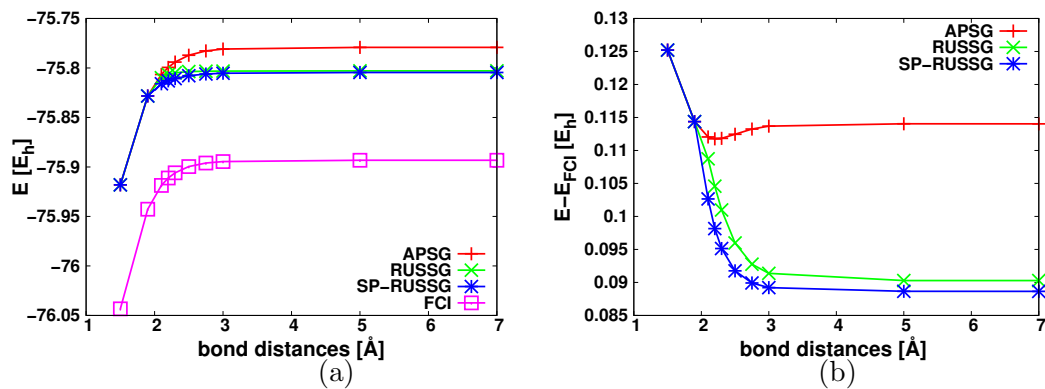


Figure 1. Total energy (panel a) and energy difference with respect to FCI (panel b) for H₂O symmetric dissociation, in 6-31G** basis set.

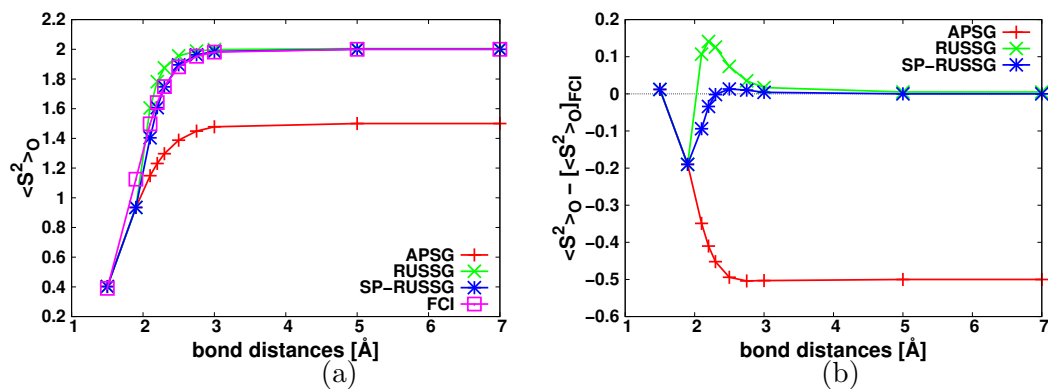


Figure 2. Local spin of oxygen (panel a) and local spin difference with respect to FCI (panel b) for H₂O symmetric dissociation, in 6-31G** basis.

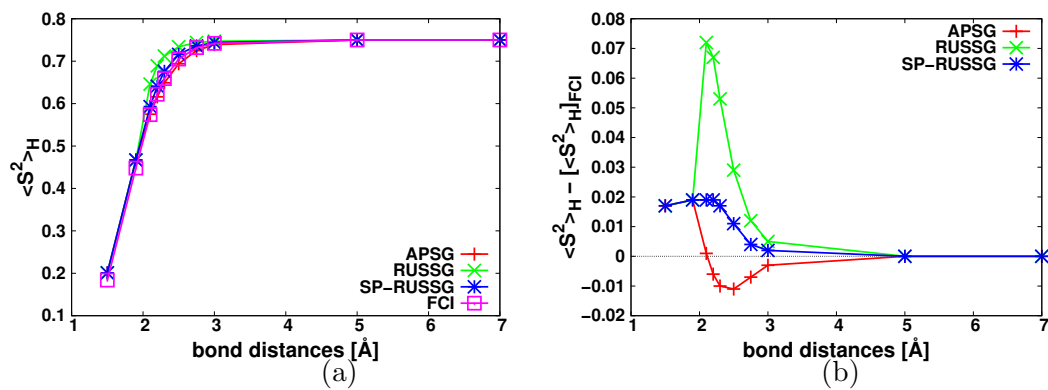


Figure 3. Local spin of hydrogen (panel a) and local spin difference with respect to FCI (panel b) for H₂O symmetric dissociation, in 6-31G** basis.

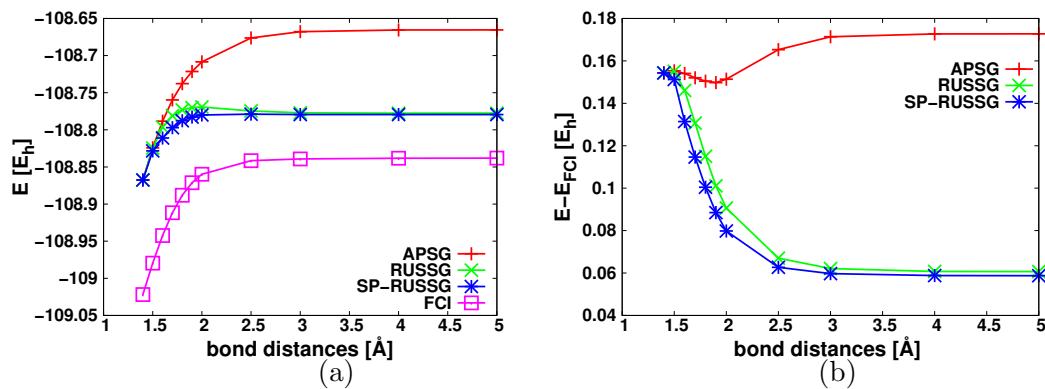


Figure 4. Total energy (panel a) and energy difference with respect to FCI (panel b) for N₂ dissociation, in 6-31G basis set.

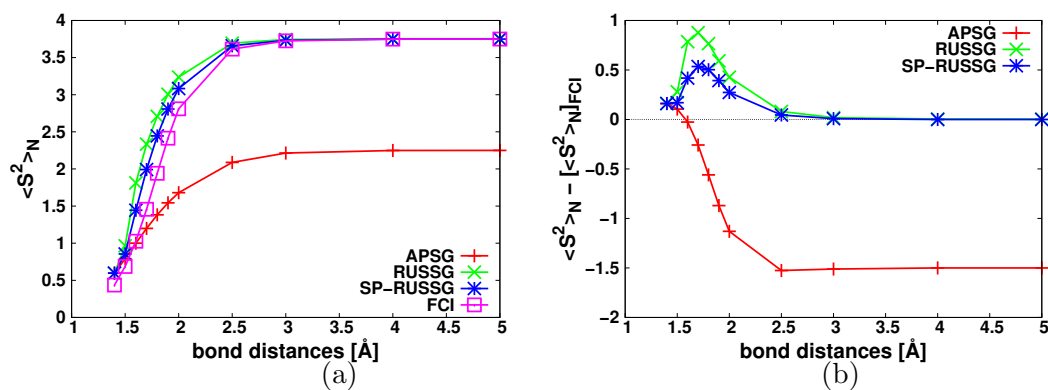


Figure 5. Local spin of nitrogen (panel a) and local spin difference with respect to FCI (panel b) for N₂ dissociation, in 6-31G basis set.

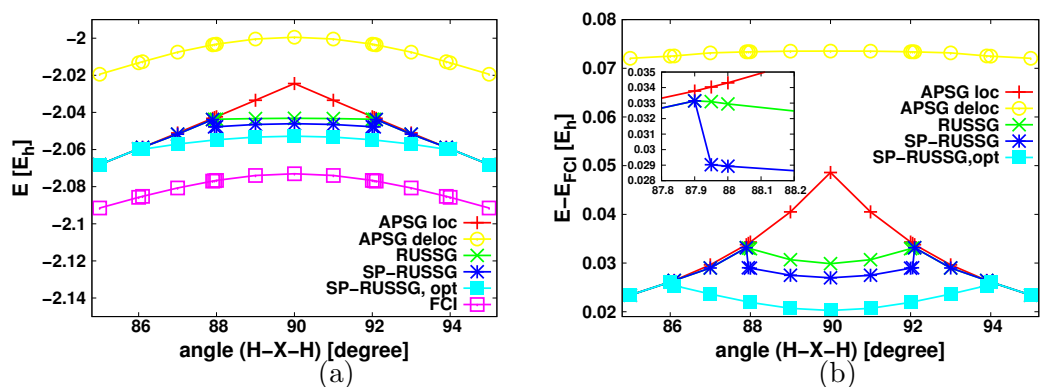


Figure 6. Total energy (panel a) and energy difference with respect to FCI (panel b) for H₄, in 6-31G** basis set. The four hydrogen atoms are confined to circle with a radius of $\sqrt{2}$ bohr. Angle of two neighboring hydrogens (H) and the center of mass (X) is labeled angle(H-X-H).

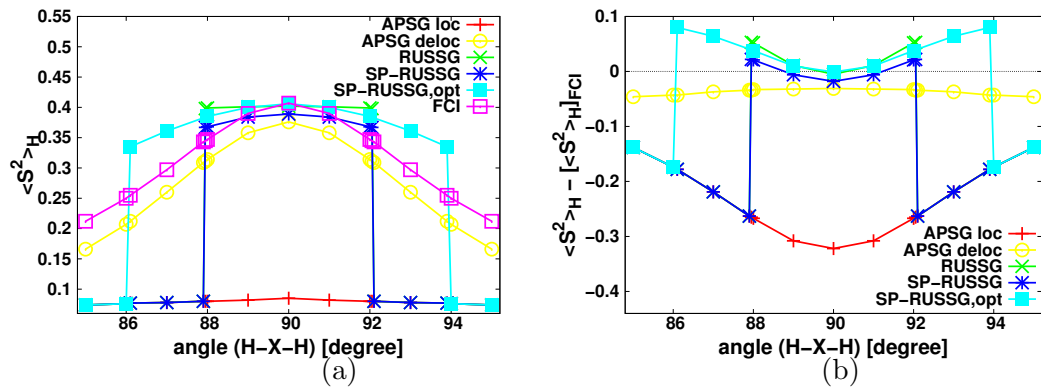


Figure 7. Local spin of hydrogen (panel a) and local spin difference with respect to FCI (panel b) for H_4 rectangular to square distortion, in 6-31G** basis set. For geometry see Fig. 6.

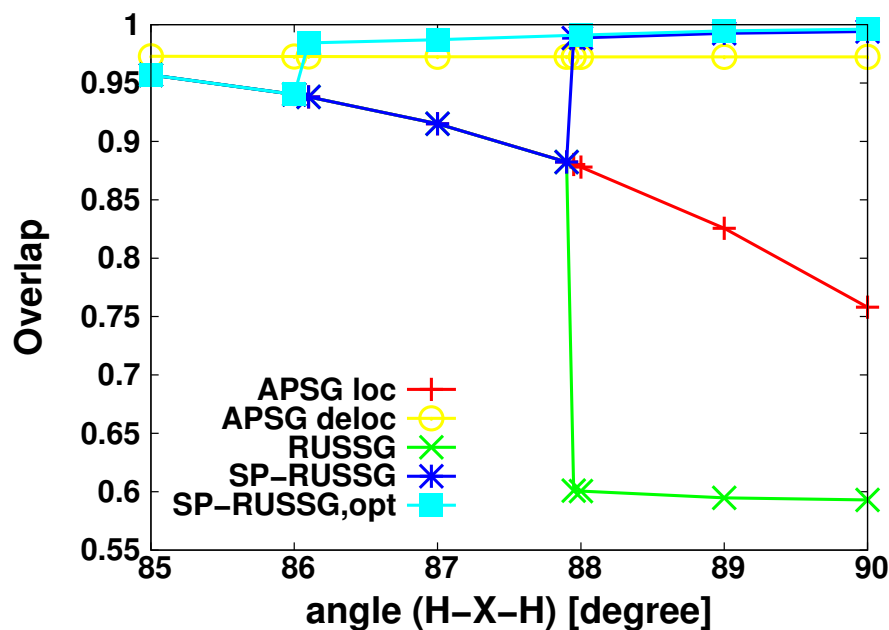


Figure 8. Overlap with the FCI vector for H_4 rectangular to square distortion, in 6-31G** basis set. For geometry see Fig. 6.

Appendix A. Analysis of local spin on the symmetric stretch of H_2O , dissociation limit

A.1. Orbitals

Assume that orthonormal orbitals o_1 and o_2 are localized on oxygen, h_1 and h_2 are localized on each hydrogen. A 45° rotation of o_1 and h_1 gives the delocalized orbitals of bonding geminal No.1:

$$\begin{aligned}\varphi_1 &= \frac{1}{\sqrt{2}}(o_1 + h_1) , \\ \varphi_2 &= \frac{1}{\sqrt{2}}(o_1 - h_1) .\end{aligned}$$

Delocalized orbitals of bonding geminal No.2, φ_3 and φ_4 , can be constructed analogously.

A.2. Geminals on OH bonds

Consider first the assignment of geminals to bonds, according to panel (a) of Fig.A1. The lowest lying singlet geminal on bond No.1 in terms of φ_1 and φ_2 looks

$$\psi_{OH1}^+ = \frac{1}{\sqrt{2}} \left(\varphi_{1\beta}^+ \varphi_{1\alpha}^+ - \varphi_{2\beta}^+ \varphi_{2\alpha}^+ \right) . \quad (\text{A1})$$

The same geminal in terms of o_1 and h_1 takes the form:

$$\psi_{OH1}^+ = \frac{1}{\sqrt{2}} \left(h_{1\beta}^+ o_{1\alpha}^+ + o_{1\beta}^+ h_{1\alpha}^+ \right) . \quad (\text{A2})$$

There are excited singlet states of bond No.1, but these are not important for the present discussion. The triplet states of bond No.1, on the other hand, are important:

$${}^3_0\psi_{OH1}^+ = \frac{1}{\sqrt{2}} \left(h_{1\beta}^+ o_{1\alpha}^+ - o_{1\beta}^+ h_{1\alpha}^+ \right) ,$$

$${}^3_{+1}\psi_{OH1}^+ = h_{1\alpha}^+ o_{1\alpha}^+ ,$$

$${}^3_{-1}\psi_{OH1}^+ = h_{1\beta}^+ o_{1\beta}^+ .$$

The case of bonding geminal No.2 is analogous.

A.3. Geminal on atom O and on HH

Consider now the assignment of geminals according to panel (b) of Fig.A1. The three triplet geminals on atom oxygen can be written as:

$${}^3_0\xi_O^+ = \frac{1}{\sqrt{2}} \left(o_{2\beta}^+ o_{1\alpha}^+ - o_{1\beta}^+ o_{2\alpha}^+ \right) ,$$

$${}^3_{+1}\xi_O^+ = o_{2\alpha}^+ o_{1\alpha}^+ ,$$

$${}^3_{-1}\xi_O^+ = o_{2\beta}^+ o_{1\beta}^+ .$$

Apart from triplets, there are three singlet states of the geminal on atom oxygen, having the form:

$${}^1\xi_O^+ = \frac{1}{\sqrt{2}} c_{21} \left(o_{2\beta}^+ o_{1\alpha}^+ + o_{1\beta}^+ o_{2\alpha}^+ \right) + c_{11} o_{1\beta}^+ o_{1\alpha}^+ + c_{22} o_{2\beta}^+ o_{2\alpha}^+ .$$

With a geminal on oxygen, it is practical to consider the unpaired electrons on the two hydrogen atoms to form either a triplet:

$${}^3_0\xi_{HH}^+ = \frac{1}{\sqrt{2}} \left(h_{2\beta}^+ h_{1\alpha}^+ - h_{1\beta}^+ h_{2\alpha}^+ \right) ,$$

$${}^3_{+1}\xi_{HH}^+ = h_{2\alpha}^+ h_{1\alpha}^+ ,$$

$${}^3_{-1}\xi_{HH}^+ = h_{2\beta}^+ h_{1\beta}^+ ,$$

or a singlet geminal:

$${}^1\xi_{HH}^+ = \frac{1}{\sqrt{2}} \left(h_{2\beta}^+ h_{1\alpha}^+ + h_{1\beta}^+ h_{2\alpha}^+ \right) .$$

The "ionic" type singlet coupling of the two hydrogen atoms ($h_{1\beta}^+ h_{1\alpha}^+ + h_{2\beta}^+ h_{2\alpha}^+$) can be neglected in the dissociation limit.

A.4. Coupling of geminal on O with geminal on HH

An overall four-electron singlet can arise by two spin-coupling schemes from the geminals on O and on HH. One can multiply a triplet with a triplet to get:

$$|DTD\rangle = \frac{1}{\sqrt{3}} \left(- {}^3_0\xi_{HH}^+ {}^3_0\xi_O^+ + {}^3_{-1}\xi_{HH}^+ {}^3_{+1}\xi_O^+ + {}^3_{+1}\xi_{HH}^+ {}^3_{-1}\xi_O^+ \right) |\text{vac}\rangle .$$

Letter D refers to doublet on hydrogen, letter T to triplet on oxygen, factors $\pm 1/\sqrt{3}$ are the Clebsch-Gordan coefficients.

It is also possible to combine a singlet with a singlet, yielding

$$|DSD\rangle = {}^1\xi_{HH}^+ {}^1\xi_O^+ |\text{vac}\rangle$$

with obvious nomenclature.

According to Hund's rule the triplet state is favored on atomic oxygen, for this reason only $|DTD\rangle$ can appear in the dissociation limit. The $|DSD\rangle$ component must tend to zero as the two hydrogens are stretched infinitely apart. Appearance of a $|DSD\rangle$ component in the dissociation limit of any approximate wavefunction gives rise to local spin contamination.

A.5. *Coupling of geminals on OH bonds*

Combination of the lowest lying singlet geminals on the OH bonds gives the APSG function:

$$|SS\rangle = |APSG\rangle = \psi_{OH_2}^+ \psi_{OH_1}^+ |\text{vac}\rangle$$

with notation S referring to the (ground state) singlet OH geminals. It is also possible to form an overall singlet combining two triplet OH geminals, giving rise to

$$|TT\rangle = \frac{1}{\sqrt{3}} \left(- {}^3_0\psi_{OH_2}^+ {}^3_0\psi_{OH_1}^+ + {}^3_{-1}\psi_{OH_2}^+ {}^3_{+1}\psi_{OH_1}^+ + {}^3_{+1}\psi_{OH_2}^+ {}^3_{-1}\psi_{OH_1}^+ \right) |\text{vac}\rangle .$$

A.6. *Local spin analysis of APSG*

Let us now analyze the APSG function from the point of view of local spin. Our goal is to express $|APSG\rangle$ in terms of $|DTD\rangle$ and $|DSD\rangle$. For this end all functions are written in terms of h_2^+, o_2^+, h_1^+ and o_1^+ , assuming the ordering $h_2 > o_2 > h_1 > o_1$.

Take first the functions built with the geminal on atom oxygen:

$$|DTD\rangle = \frac{1}{\sqrt{3}} \left(\frac{1}{2} h_{2\beta}^+ o_{2\beta}^+ h_{1\alpha}^+ o_{1\alpha}^+ + \frac{1}{2} o_{2\beta}^+ h_{1\beta}^+ h_{2\alpha}^+ o_{1\alpha}^+ + h_{2\beta}^+ h_{1\beta}^+ o_{2\alpha}^+ o_{1\alpha}^+ + \{\text{spin-flip}\} \right),$$

$$|DSD\rangle = \frac{1}{\sqrt{2}} \left[\frac{c_{21}}{\sqrt{2}} \left(-h_{2\beta}^+ o_{2\beta}^+ h_{1\alpha}^+ o_{1\alpha}^+ + o_{2\beta}^+ h_{1\beta}^+ h_{2\alpha}^+ o_{1\alpha}^+ \right) - c_{11} h_{2\beta}^+ o_{1\beta}^+ h_{1\alpha}^+ o_{1\alpha}^+ \right. \\ \left. + c_{22} h_{2\beta}^+ o_{2\beta}^+ o_{2\alpha}^+ h_{1\alpha}^+ + \{\text{spin-flip}\} \right].$$

Notation "spin-flip" refers to substituting α for β and vice versa.

Take now the functions derived from bonding geminals:

$$|TT\rangle = \frac{1}{\sqrt{3}} \left(h_{2\beta}^+ o_{2\beta}^+ h_{1\alpha}^+ o_{1\alpha}^+ - \frac{1}{2} o_{2\beta}^+ h_{1\beta}^+ h_{2\alpha}^+ o_{1\alpha}^+ + \frac{1}{2} h_{2\beta}^+ h_{1\beta}^+ o_{2\alpha}^+ o_{1\alpha}^+ + \{\text{spin-flip}\} \right),$$

$$|SS\rangle = -\frac{1}{2} \left(o_{2\beta}^+ o_{1\beta}^+ h_{2\alpha}^+ h_{1\alpha}^+ + o_{2\beta}^+ h_{1\beta}^+ h_{2\alpha}^+ o_{1\alpha}^+ + \{\text{spin-flip}\} \right).$$

Scalar products of $|SS\rangle$ with $|DTD\rangle$ and $|DSD\rangle$ are $-\sqrt{3}/2$ and $-c_{21}/2$, respectively. Since $c_{21} = 1$ (and $c_{11} = c_{22} = 0$) for the lowest singlet state of atomic oxygen, the APSG wavefunction in the dissociation limit takes the form

$$|APSG\rangle = -\frac{\sqrt{3}}{2} |DTD\rangle - \frac{1}{2} |DSD\rangle.$$

This results

$$\langle APSG | \hat{S}^2 | APSG \rangle_O = \left(\frac{\sqrt{3}}{2} \right)^2 1(1+1) + \left(\frac{1}{2} \right)^2 0(0+1) = \frac{3}{2}$$

instead of the correct value, 2.

Putting in other terms, one can express the FCI wavefunction in the dissociation limit (i.e. $|DTD\rangle$) with $|SS\rangle$ and $|TT\rangle$ to get

$$|FCI\rangle = -\frac{\sqrt{3}}{2} |SS\rangle + \frac{1}{2} |TT\rangle.$$

This reveals that the product of triplet OH geminals, omitted from APSG, has a considerable weight in the correct limiting wavefunction.

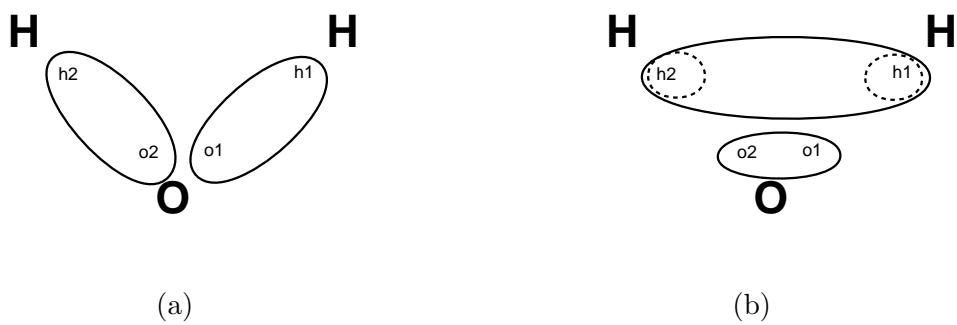


Figure A1. Assignment schemes of bonding electron pairs to geminals in H_2O .