Determination of Heisenberg Exchange Coupling Constants in Clusters with Magnetic Sites: A Local Spin Approach

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This work studies the ability of the two-center local spin quantities, provided by the partitioning of the expectation value of the spin-squared operator $<\hat{S}^2>$ corresponding to *N*-electron systems, for determining spin-exchange coupling constants within the Heisenberg spin Hamiltonian model. The spin-exchange parameters, which characterize this Hamiltonian for a determined system, have been evaluated in the HeH_2 aggregate and in several H_n clusters ($n = 2$, 3, 4) with different geometrical arrangements, using internuclear distances larger than the equilibrium ones (beyond the bonding regions). The results found have been analyzed and compared with those arising from other approaches, showing the feasibility of our methodology. © 2014 Wiley Periodicals, Inc.

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Introduction

The partitioning of the values of a determined molecular property into contributions which can be assigned to atoms or groups of atoms which compose an *N*-electron system has proven to be a very useful technique in molecular physics and quantum chemistry. The number of electrons *N*, the electronic energy, the electron density and so forth have been decomposed according to the fragments of the molecular system, providing interesting insights into its molecular structure and its atomic bondings. Another property studied within this scheme is the expectation value of the spin-squared operator $<\hat{S}^2>$ corresponding to a state of an *N*-electron system. The partitioning of the $<\hat{S}^2>$ quantity into one- and two-center terms (local spins) allows one to know the spin state of an atom or group of atoms within a molecular system and to describe the magnetic interactions between its centers. The task of dividing suitably the spin values $<\hat{S}^2>$ has been tackled through several procedures. Some authors have proposed the use of atomic projection operators associated with the nuclei of the system,[1–7] while others have undertaken a direct partitioning of the $<\hat{S}^2>$ quantity.[8–18] Although the results provided by both partitioning types have been widely discussed, their local spin values have scarcely been utilized to determine magnetic properties in the studied systems.[4,9,19]

On the other hand, the phenomenological Heisenberg spin Hamiltonian has successfully been applied in many areas of chemistry and material science to describe relative energies of the states arising from different spin couplings in compounds containing unpaired electrons.[20] A rigorous determination of the coupling constants of this operator from *ab initio* wave functions requires the use of symmetry-adapted functions that involves a high-computational cost. Consequently, different approximated computational procedures have been proposed[21–24] to perform this task; most of them are based on the use of the energies arising from the high-spin (HS) and broken-symmetry (BS) determinants. This picture provides an intuitive insight into the magnetic interactions in terms of ferromagnetic and antiferromagnetic couplings, although the use of the BS determinants implies a spin contamination in the results obtained. In the approaches reported by Noodleman[21,22] and Yamaguchi and coworkers,[23–26] the evaluation of coupling constants is carried out through the difference of the total spin expectation values $<\hat{S}^2>$ corresponding to the HS and BS determinants. However, in multispin systems the evaluation of these coupling constants has required the use of

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two-center local spin values, which have been calculated by means of different averages of the one-center local spin ones,[4–26] or perturbative approaches.[27] The aim of this work is to carry out a study of the capability of two-center local spins arising from the direct partitioning of the $<\hat{S}^2>$ quantity to determine coupling constants in different situations which have not been examined, to our knowledge, in a systematic manner. To perform this task, we consider systems possessing two or more magnetic sites which exhibit one, two, or three equal or different coupling constants. To implement this study, we have chosen the HeH_2 and H_n ($n = 2, 3, 4$) clusters at different geometrical arrangements, using stretched internuclear distances. These clusters have been considered as simple prototype systems which present several spin coupling constants and have also been described within other approaches.[28,29]

The organization of this work is as follows. The second section describes the procedure utilized to evaluate the coupling constants, within the framework of the Heisenberg spin Hamiltonian, in the studied systems, as well as the formulations used in other treatments. This section also reports the direct partitioning of the expectation value of the spin-squared operator $<\hat{S}^2>$ and the formulation of one- and two-center local spins resulting from that division. In third section, we show the computational aspects, the numerical values obtained and the corresponding discussion as well as a comparison between our results and those arising from other methods. Finally, in the last section we highlight the conclusions of this work.

Theoretical Review

As is well-known, the Heisenberg spin Hamiltonian model has been formulated as

$$\hat{H} = E_0 - 2\sum_{A<B} J_{AB}\,\hat{S}_A\hat{S}_B \tag{1}$$

where E_0 is a constant meaning the origin of the energy scale chosen for that model, $A, B, \ldots$ are the magnetic sites within the system, J_{AB} the coupling constant between them and $\hat{S}_A$ and $\hat{S}_B$ the spin operators assigned to those centers. In Noodleman's treatment,[21] the expectation values of the Hamiltonian $\hat{H}$ in Eq. (1) are calculated through Slater determinants. One of these determinants is the highest pure spin multiplet (HS) in which all its orbitals are singly occupied with spin up (a ferromagnetic disposal). The other determinants are mixed spin symmetry and lowered spin symmetry; they are denominated BS states possessing singly occupied orbitals with spin down (an antiferromagnetic disposal). Consequently, the differences of the energies $(E^{HS} - E^{BS})$ corresponding to the determinants are

$$E^{HS} - E^{BS} = -2\sum_{A<B} J_{AB}\left[<\hat{S}_A\hat{S}_B>^{HS} - <\hat{S}_A\hat{S}_B>^{BS}\right] \tag{2}$$

There are different possibilities to formulate the BS determinants so that Eq. (2) constitutes a system of linear equations in the variables J_{AB} provided that the two-center expectation values $<\hat{S}_A\hat{S}_B>^{HS}$ and $<\hat{S}_A\hat{S}_B>^{BS}$ have previously been evaluated.

Taking into account the decomposition of the spin-squared operator $\hat{S}^2 = (\sum_A \hat{S}_A)^2$ between its one- and two-center spin operators associated with these centers, one can formulate

$$<\hat{S}^2> = \sum_A <\hat{S}_A^2> + 2\sum_{A<B} <\hat{S}_A\hat{S}_B> \tag{3}$$

and assuming identical one-center terms $<\hat{S}_A^2>$ values for both HS and BS states[23,25] ($<\hat{S}_A^2>^{HS} \approx <\hat{S}_A^2>^{BS}$ as applicability condition) one can relate differences of total spins to differences of two-center local spins

$$<\hat{S}^2>^{HS} - <\hat{S}^2>^{BS} = 2\sum_{A<B}\left[<\hat{S}_A\hat{S}_B>^{HS} - <\hat{S}_A\hat{S}_B>^{BS}\right] \tag{4}$$

For a system with two magnetic centers, Yamaguchi and coworkers[23,25] formulated the unique coupling constant J_{AB} according to Eqs. (2) and (4), resulting

$$J_{AB} = -\frac{E^{HS} - E^{BS}}{<\hat{S}^2>^{HS} - <\hat{S}^2>^{BS}} \tag{5}$$

Afterward, this treatment was generalized to multispin systems involving a more sophisticated formulation.[26]

Alternatively, the determination of J_{AB} parameters can be addressed through a rigorous calculation of the two-center local spins.[4,9,19] As mentioned in the Introduction, the purpose of this work is to know the capabilities of two-center local spins derived from the direct partitioning model of the expectation value of the spin-squared operator $<\hat{S}^2>$ according to[8,10,12,14–17]

$$<\hat{S}^2> = \sum_A <\hat{S}^2>_A + 2\sum_{A<B} <\hat{S}^2>_{AB} \tag{6}$$

to evaluate coupling constants within the Heisenberg spin Hamiltonian. According to this purpose, the terms $<\hat{S}_A^2>$ and $<\hat{S}_A\hat{S}_B>$ (arising from the spin atomic operator formulation) will be identified, respectively, with those $<\hat{S}^2>_A$ and $<\hat{S}^2>_{AB}$ (arising from the direct partitioning of $<\hat{S}^2>$ of Eq. (6)), as was proposed in Ref. [8]. In this work, we will use local spins arising from our direct partitioning of $<\hat{S}^2>$ quantity in the Hilbert space.[15] In the case of states described by Slater determinants, this partitioning leads to

$$<\hat{S}^2>_{AB} = \frac{1}{4}\sum_{\mu\in A}\sum_{\nu\in B}(P^s\mathbb{S})_{\mu\mu}(P^s\mathbb{S})_{\nu\nu} + \delta_{AB}\,\frac{1}{2}\sum_{\mu\in A}\sum_{\nu\in B}(P^s\mathbb{S})_{\mu\nu}(P^s\mathbb{S})_{\nu\mu} \tag{7}$$

Equation (7) represents both one- and two-center local spin terms in a compact formula by means of the Kronecker delta δ_{AB}. In this formula, $\mu, \nu, \ldots$ are the atomic orbitals, $\mathbb{S}$ is their overlap matrix, and $P^s = P^\alpha - P^\beta$ is the spin density resulting from the decomposition of the cumulant matrix (P^α and P^β are the α- and β-blocks of the first-order reduced density matrix respectively); in this relationship, the sums are restricted to the

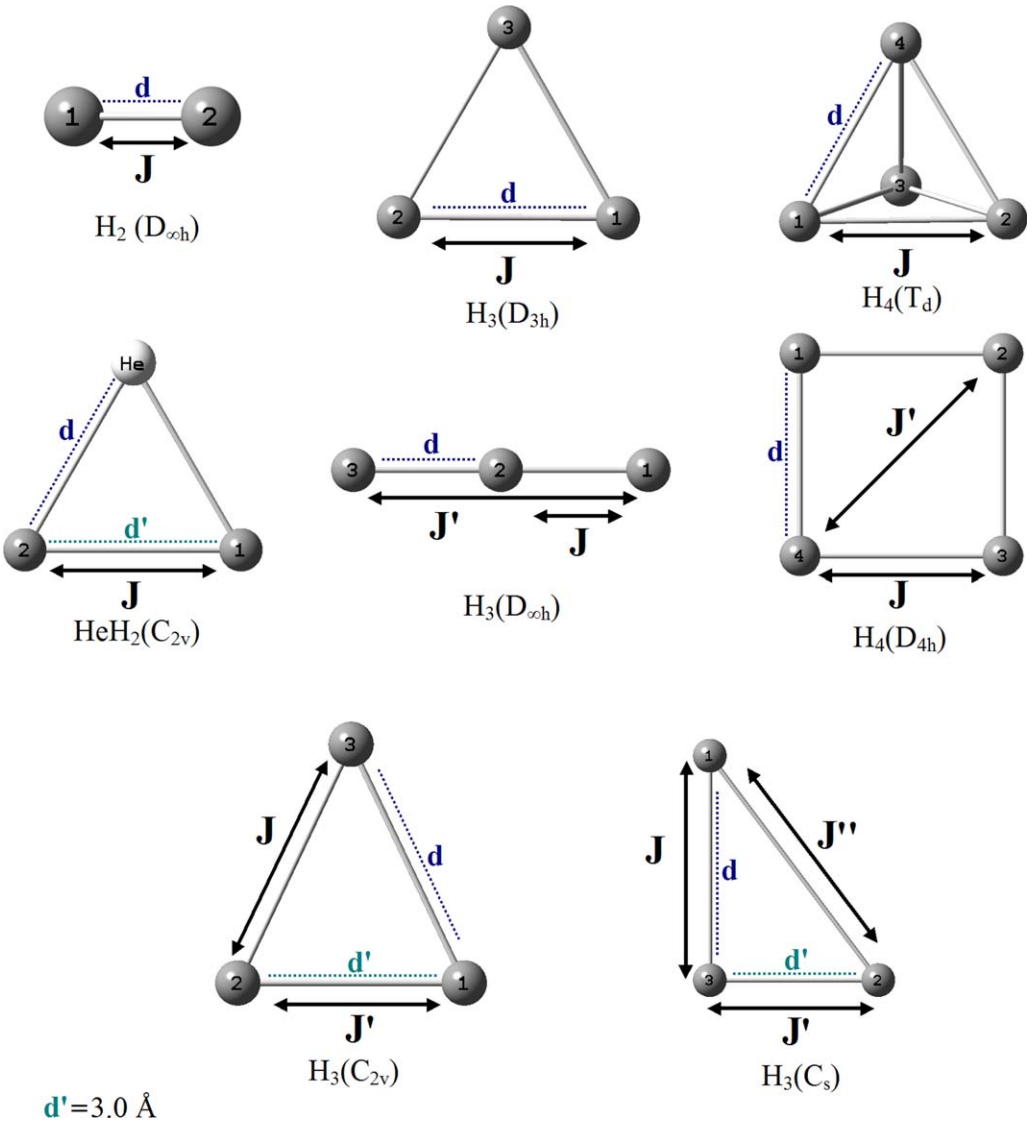

Figure 1. Point groups and geometrical distances of the systems studied in this work. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

atomic functions assigned to the corresponding center. The determination of the two-center local spins $<\hat{S}^2>_{AB}^{HS}$ and $<\hat{S}^2>_{AB}^{BS}$ according to formula (7) and their introduction in the system of equations given in Eq. (2) allow one to calculate the J_{AB} parameters in systems possessing one or several identical or different spin coupling constants. Alternatively, values of the two-center local spins $<\hat{S}^2>_{AB}^{HS}$ and $<\hat{S}^2>_{AB}^{BS}$ arising from other direct partitionings of the quantity $<\hat{S}^2>$ could be utilized.[8,16,17] In the next section, we report results arising from the application of this methodology to several Hydrogen clusters with different geometrical arrangements which represent a variety of situations and interactions between their magnetic sites.

Results and Discussion

The determination of energies E^{HS} and E^{BS} required in Eq. (2) has been performed at unrestricted Hartree–Fock (UHF) and unrestricted Becke-3-parameter-Lee-Yang-Parr (UB3LYP) functional levels, using the GAUSSIAN 09 package[30] and the atomic basis sets STO-3G, 6–31G, 6–31G(d,p), and cc-pVTZ. Likewise, with that package we have evaluated the spin-density matrix elements P^s and the overlap integrals $\mathbb{S}$ needed in Eq. (7). The calculation of the two-center local spins $<\hat{S}^2>_{AB}$ has been carried out, in subsequent steps, using our own codes. The solutions of the systems of linear equations expressed by Eq. (2) have been obtained using MATHEMATICA 9.0.[31] We have constructed these systems of equations with each of the determinants of type BS which represent all possible spin orientations of the individual centers plus the determinant which describes the HS state. We have evaluated the different coupling constants J_{AB} (as well as the E_0 quantity) in the systems $H_2(D_{\infty h})$, $H_3(D_{3h})$, $H_4(T_d)$, $HeH_2(C_{2v})$, $H_3(D_{\infty h})$, $H_4(D_{4h})$, $H_3(C_{2v})$, and $H_3(C_s)$, at different internuclear distances. The Hydrogen atoms which compose all these systems were situated at distances much longer than the equilibrium one in

Table 1. Values (in cm^{-1}) of the coupling constants J, J', and J'' for Hydrogen clusters at stretched distances H—H (d/Å) and $d' = 3.0$ Å (see Fig. 1).

	$H_2(D_{\infty h})$	$H_3(D_{3h})$	$H_4(T_d)$	$HeH_2(C_{2v})$	$H_3(D_{\infty h})$		$H_4(D_{4h})$		$H_3(C_{2v})$		$H_3(C_s)$		
d/Å	J	J	J	J	J	J'	J	J'	J	J'	J	J'	J''
2.0	−2839	−2395	−1686	−13.74	−2881	−19.25	−2708	12.92	−2804	−5.068	−2837	−73.73	−2.696
2.2	−1416	−1248	−1001	−44.13	−1428	−5.437	−1376	2.886	−1386	−35.04	−1415	−75.03	−1.679
2.4	−700.8	−639.4	−553.3	−61.48	−703.7	−1.624	−689.4	0.182	−682.6	−54.68	−700.1	−75.67	−1.087
2.6	−342.1	−320.5	−293.1	−69.93	−342.8	−0.345	−338.8	−0.298	−332.3	−65.73	−341.6	−76.01	−0.697
2.8	−163.7	−156.5	−147.5	−73.75	−163.8	−0.070	−162.8	−0.203	−158.8	−71.41	−163.4	−76.24	−0.401
3.0	−76.46	−74.17	−71.56	−75.38	−76.49	−0.026	−76.24	−0.093	−74.17	−74.17	−76.34	−76.34	−0.229
3.225	−31.47	−30.88	−30.26	−76.24	−31.48	0.003	−31.43	−0.029	−30.53	−75.55	−31.41	−76.41	−0.110
3.5	−10.17	−10.06	−11.46	−76.40	−10.17	0.001	−10.16	−0.005	−9.870	−76.18	−10.15	−76.44	−0.044
4.0	−1.115	−1.089	−1.149	−76.45	−1.156	0.000	−1.156	−0.000	−1.124	−76.43	−1.154	−76.46	−0.006
5.0	−0.008	−0.009	−0.010	−76.46	−0.009	0.000	−0.009	−0.000	−0.009	−76.46	−0.009	−76.46	0.000

Results correspond to UHF level using STO-3G basis sets. (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

the H_2 molecule and consequently, all the electrons around the Hydrogen atoms can be regarded as magnetic active centers. The geometrical arrangements of these clusters are shown in Figure 1. In the case of $HeH_2(C_{2v})$ cluster, we pretend to study the influence of the He atom on the stretched H_2 molecule (at $d'_{H\text{-}H} = 3$ Å) scanning the distances $d_{H\text{-}He}$ (see Fig. 1). In the $H_4(D_{4h})$ cluster case, a singular value decomposition was used to solve the resulting overdetermined system of linear equations,[29] which arises from considering four α centers, three α and one β centers, and two α and two β centers set out in diagonal and neighbor positions. The cluster $H_4(T_d)$ presents similar features, although to compare our results with those arising from the Yamaguchi approach only two states (the lowest energy ones) have been considered.

Tables 1 and 2 report values of the coupling constants calculated at different internuclear distances d (see Fig. 1) for the mentioned clusters described at UHF level in the basis sets STO-3G and 6–31G(d,p), respectively. We have grouped the systems according to the number of coupling constants having a different value; a unique value ($H_2(D_{\infty h})$, $H_3(D_{3h})$, $H_4(,T_d)$ and $HeH_2(C_{2v})$), two different values ($H_3(D_{\infty h})$, $H_4(D_{4h})$, and $H_3(C_{2v})$) and three different ones ($H_3(C_s)$). A survey of the results contained in these Tables shows a strong dependence of the coupling constant values on the internuclear distances; this feature is exhibited as in the minimum basis sets as in the larger 6–31G(d,p) ones. Starting with the $H_2(D_{\infty h})$ molecule, the reference system, this dependence shows an exponential decay as expected.[32] For internuclear distances between the interacting centers considered $d_{H\text{-}H} \approx 3$ Å and longer ones (beyond the bonding region), all the H_n ($n = 2, 3, 4$) clusters present similar values for their corresponding J constants involving those centers, for both basis sets. The clusters $HeH_2(C_{2v})$, $H_3(C_{2v})$, and $H_3(C_s)$ also present this feature for the values of J (in the HeH_2 cluster) and J' (in the $H_3(C_{2v})$ and $H_3(C_s)$ ones). These coupling constants correspond to interactions between two H centers maintained at the fixed distance d' of 3 Å (see Fig. 1), while the distance d of these two centers to another atom (He in the $HeH_2(C_{2v})$ cluster and H in the $H_3(C_{2v})$ and $H_3(C_s)$ ones) is scanned. The value of J for $H_2(D_{\infty h})$ at the internuclear distance of 3 Å is the reference for these cases. The obtained values point out that the interaction between two adjacent magnetic centers is affected by their distance to a third atom, even in the case of the diamagnetic He one. The J'' value of the $H_3(C_s)$ also performs according to those patterns. The J' values in the clusters $H_3(D_{\infty h})$ and $H_4(D_{4h})$ represent interactions between two nonadjacent centers and two diagonally placed centers, respectively; the reported values reflect simultaneously the effect of the distances between both centers and from those to their neighbors. Consequently, one can conclude that our proposal for evaluating Heisenberg coupling constants by means of the two-center local spins reported in Eq. (7), in Hydrogen clusters,

Table 2. Values (in cm^{-1}) of the coupling constants J, J', and J'' for Hydrogen clusters at stretched distances H—H (d/Å) and $d' = 3.0$ Å (see Fig. 1).

	$H_2(D_{\infty h})$	$H_3(D_{3h})$	$H_4(T_d)$	$HeH_2(C_{2v})$	$H_3(D_{\infty h})$		$H_4(D_{4h})$		$H_3(C_{2v})$		$H_3(C_s)$		
d/Å	J	J	J	J	J	J'	J	J'	J	J'	J	J'	J''
2.0	−3285	−2572	−1470	−10.89	−3385	−94.77	−3046	−26.26	−3181	−14.18	−3278	−144.1	−5.090
2.2	−1802	−1472	−999.0	−70.91	−1839	−32.32	−1711	0.505	−1719	−51.47	−1798	−149.4	−4.014
2.4	−987.2	−838.4	−637.0	−111.5	−999.4	−10.15	−953.0	2.825	−931.9	−91.19	−984.4	−152.9	−3.073
2.6	−538.5	−474.1	−391.2	−135.0	−542.1	−2.958	−526.4	1.396	−505.3	−119.8	−536.8	−155.1	−2.208
2.8	−292.3	−265.9	−232.7	−147.3	−293.3	−0.769	−288.4	0.356	−273.6	−137.3	−291.3	−156.4	−1.452
3.0	−157.8	−147.6	−135.1	−153.3	−158.0	−0.144	−156.6	0.028	−147.6	−147.6	−157.2	−157.2	−0.921
3.225	−77.97	−74.78	−70.90	−156.2	−78.02	−0.001	−77.74	−0.024	−73.01	−153.5	−77.64	−157.6	−0.528
3.5	−32.14	−31.49	−31.08	−157.4	−32.15	0.008	−32.12	−0.016	−30.18	−156.5	−32.00	−157.7	−0.243
4.0	−5.700	−5.684	−5.686	−157.8	−5.701	0.001	−5.701	−0.001	−5.395	−157.7	−5.675	−157.8	−0.050
5.0	−0.085	−0.085	−0.084	−157.8	−0.085	0.000	−0.085	0.000	−0.082	−157.8	−0.085	−157.8	−0.001

Results correspond to UHF level using 6–31G(d,p) basis sets. (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

Table 3. Values (in cm^{-1}) of the coupling constants J, J', and J'' for Hydrogen clusters at stretched distances H—H (d/Å) and $d' = 3.0$ Å (see Fig. 1).

	$H_2(D_{\infty h})$	$H_3(D_{3h})$	$H_4(T_d)$	$HeH_2(C_{2v})$	$H_3(D_{\infty h})$		$H_4(D_{4h})$		$H_3(C_{2v})$		$H_3(C_s)$		
d/Å	J	J	J	J	J	J′	J	J′	J	J′	J	J′	J″
2.0	−5543	−4699	−2733	−68.57	−5707	32.74	−5156	66.13	−5548	−13.47	−5539	−196.9	−17.69
2.2	−2769	−2487	−1800	−131.3	−2830	30.01	−2702	37.79	−2746	−85.17	−2767	−200.5	−12.47
2.4	−1421	−1319	−1096	−168.9	−1440	11.54	−1405	4.808	−1397	−150.8	−1419	−202.3	−8.865
2.6	−739.6	−701.7	−630.8	−188.0	−745.6	3.529	−733.7	−3.582	−723.1	−180.5	−738.2	−203.2	−6.528
2.8	−387.9	−374.7	−351.4	−197.1	−389.2	1.791	−385.0	−3.637	−378.3	−193.4	−386.5	−203.3	−4.196
3.0	−204.7	−199.1	−191.8	−201.1	−204.6	1.092	−203.2	−2.175	−199.1	−199.1	−203.6	−203.6	−3.665
3.225	−100.4	−97.32	−95.99	−202.9	−100.5	0.200	−99.71	−1.019	−97.51	−202.0	−99.70	−204.0	−2.313
3.5	−42.85	−41.12	−41.36	−203.9	−42.90	0.037	−42.59	−0.404	−41.33	−203.4	−42.39	−204.2	−1.270
4.0	−9.406	−9.246	−9.069	−204.5	−9.399	0.002	−9.356	−0.050	−9.044	−204.2	−9.116	−204.4	−0.520
5.0	−0.441	−0.447	−0.435	−204.7	−0.446	0.000	−0.446	−0.000	−0.414	−204.7	−0.254	−204.5	−0.206

Results correspond to UB3LYP level using STO-3G basis sets. (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

Table 4. Values (in cm^{-1}) of the coupling constants J, J', and J'' for Hydrogen clusters at stretched distances H—H (d/Å) and $d' = 3.0$ Å (see Fig. 1).

	$H_2(D_{\infty h})$	$H_3(D_{3h})$	$H_4(T_d)$	$HeH_2(C_{2v})$	$H_3(D_{\infty h})$		$H_4(D_{4h})$		$H_3(C_{2v})$		$H_3(C_s)$		
d/Å	J	J	J	J	J	J′	J	J′	J	J′	J	J′	J″
2.0	−6775	−5298	−2372	−129.4	−6947	−249.8	−5733	−244.6	−6573	−174.2	−6767	−409.2	−54.30
2.2	−3727	−3129	−1846	−257.6	−3828	−21.00	−3446	−27.75	−3607	−194.2	−3719	−430.4	−38.28
2.4	−2136	−1878	−1326	−346.3	−2173	1.700	−2043	−15.92	−2049	−304.0	−2129	−439.2	−28.92
2.6	−1256	−1143	−912.3	−398.4	−1268	2.216	−1220	−16.55	−1200	−373.3	−1251	−444.4	−21.74
2.8	−750.5	−702.1	−607.0	−426.2	−754.0	1.180	−734.8	−12.74	−715.7	−410.8	−746.4	−447.1	−15.92
3.0	−451.7	−431.5	−393.8	−439.8	−452.8	0.570	−444.6	−7.853	−431.5	−431.5	−448.3	−448.3	−11.59
3.225	−255.2	−247.7	−235.0	−446.5	−255.4	0.194	−252.0	−3.975	−244.4	−443.1	−252.9	−449.8	−7.266
3.5	−125.3	−123.3	−119.5	−449.6	−125.3	0.017	−124.1	−1.612	−120.0	−448.5	−124.0	−450.8	−3.888
4.0	−31.77	−31.66	−30.75	−451.0	−31.68	−0.008	−31.50	−0.225	−30.16	−450.5	−31.09	−451.5	−1.150
5.0	−1.519	−1.523	−1.490	−451.6	−1.534	−0.000	−1.533	−0.001	−1.426	−451.8	−1.497	−451.9	−0.085

Results correspond to UB3LYP level using 6–31G(d,p) basis sets. (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

leads to J_{HH} values which turn out to be transferable from the simplest $H_2(D_{\infty h})$ molecule to more sophisticated H_n clusters, in different geometrical arrangements, at distances longer than 3 Å between two neighbor atoms. These numerical determinations agree with the conclusions reported in Ref. [28] for this type of systems, which were described by means of analytical solutions at full configuration interaction level, requiring a considerably higher computational expense. In Tables 3 and 4, we report results arising from an identical methodological study of those systems, described at UB3LYP level in the STO-3G and 6–31G(d,p) basis sets. As can be observed, the results in these Tables, compared with their counterparts in Tables 1 and 2, reveal a strong influence of the electron correlation. Previous studies have reported that density functional theory methods typically overestimate J values,[29,33,34] as confirmed in the present results. Although the coupling constant values found differ significantly from the minimum basis sets to larger ones[28] and from the uncorrelated level to correlated one,

Table 5. Values (in cm^{-1}) of the coupling constant J for the $H_2(D_{\infty h})$ molecule at stretched distances H—H (d/Å) and UHF and UB3LYP theory levels, using STO-3G, 6–31G, 6–31G(d,p), and cc-pVTZ basis sets.

	UHF				UB3LYP			
d/Å	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ
2.0	−2839 (−2639)	−3297 (−2931)	−3285 (−2918)	−3291 (−2920)	−5543 (−4309)	−6795 (−4594)	−6775 (−4575)	−6906 (−4573)
2.2	−1416 (−1365)	−1812 (−1695)	−1802 (−1686)	−1822 (−1705)	−2769 (−2449)	−3741 (−3006)	−3727 (−2991)	−3820 (−3023)
2.4	−700.8 (−688.4)	−993.6 (−957.3)	−987.2 (−950.9)	−1009 (−972.3)	−1421 (−1340)	−2144 (−1904)	−2136 (−1892)	−2208 (−1937)
2.6	−342.1 (−339.1)	−542.9 (−531.7)	−538.5 (−527.2)	−555.9 (−544.6)	−739.6 (−719.3)	−1262 (−1175)	−1256 (−1175)	−1315 (−1221)
2.8	−163.7 (−163.0)	−295.1 (−291.7)	−292.3 (−288.9)	−304.2 (−300.7)	−387.9 (−383.0)	−754.2 (−727.3)	−750.5 (−723.7)	−800.2 (−767.8)
3.0	−76.46 (−76.30)	−159.3 (−158.2)	−157.8 (−156.7)	−165.1 (−164.0)	−204.7 (−203.5)	−453.5 (−444.7)	−451.7 (−442.8)	−495.6 (−484.1)
3.225	−31.47 (−31.45)	−78.62 (−78.37)	−77.97 (−77.72)	−82.13 (−81.86)	−100.4 (−100.2)	−255.9 (−253.4)	−255.2 (−252.7)	−294.6 (−291.0)
3.5	−10.17 (−10.16)	−32.33 (−32.29)	−32.14 (−32.10)	−34.51 (−34.46)	−42.85 (−42.82)	−125.5 (−125.0)	−125.3 (−124.8)	−159.9 (−158.9)
4.0	−1.115 (−1.115)	−5.713 (−5.712)	−5.700 (−5.699)	−6.969 (−6.966)	−9.406 (−9.406)	−31.77 (−31.75)	−31.77 (−31.75)	−55.53 (−55.45)
5.0	−0.008 (−0.009)	−0.085 (−0.085)	−0.085 (−0.085)	−0.282 (−0.282)	−0.441 (−0.441)	−1.519 (−1.519)	−1.519 (−1.519)	−7.201 (−7.200)

In parenthesis, the Yamaguchi values arising from Eq. (5). (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

Table 6. Values (in cm^{-1}) of the coupling constant J for the $H_3(D_{3h})$ cluster at stretched distances H—H (d/Å) and UHF and UB3LYP theory levels using STO-3G, 6–31G, 6–31G(d,p), and cc-pVTZ basis sets.

	UHF				UB3LYP			
d/Å	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ
2.0	−2395 (−2251)	−2582 (−2353)	−2572 (−2343)	−2554 (−2324)	−4699 (−3820)	−5311 (−3980)	−5298 (−3963)	−5329 (−3935)
2.2	−1248 (−1208)	−1479 (−1401)	−1472 (−1394)	−1469 (−1392)	−2487 (−2227)	−3139 (−2625)	−3129 (−2614)	−3153 (−2613)
2.4	−639.4 (−628.9)	−843.8 (−817.1)	−838.4 (−811.8)	−843.0 (−817.1)	−1319 (−1248)	−1886 (−1697)	−1878 (−1689)	−1904 (−1702)
2.6	−320.5 (−317.8)	−478.0 (−469.1)	−474.1 (−465.3)	−479.8 (−471.3)	−701.7 (−683.2)	−1149 (−1081)	−1143 (−1076)	−1169 (−1095)
2.8	−156.5 (−155.8)	−268.4 (−265.5)	−265.9 (−263.0)	−270.1 (−267.4)	−374.7 (−370.0)	−704.9 (−681.2)	−702.1 (−678.3)	−729.1 (−701.9)
3.0	−74.17 (−74.02)	−148.9 (−148.0)	−147.6 (−146.6)	−150.2 (−149.3)	−199.1 (−198.2)	−433.1 (−424.9)	−431.5 (−423.3)	−460.3 (−450.3)
3.225	−30.88 (−30.86)	−75.39 (−75.14)	−74.78 (−74.54)	−76.11 (−75.88)	−97.32 (−97.08)	−249.0 (−246.6)	−247.7 (−245.3)	−278.2 (−274.9)
3.5	−10.06 (−10.06)	−31.67 (−31.63)	−31.49 (−31.44)	−32.83 (−32.78)	−41.12 (−41.09)	−124.1 (−123.6)	−123.3 (−122.8)	−153.6 (−152.7)
4.0	−1.089 (−1.089)	−5.697 (−5.695)	−5.684 (−5.682)	−6.747 (−6.744)	−9.246 (−9.246)	−31.47 (−31.44)	−31.66 (−31.63)	−54.16 (−54.07)
5.0	−0.009 (−0.009)	−0.085 (−0.085)	−0.085 (−0.085)	−0.279 (−0.279)	−0.447 (−0.447)	−1.523 (−1.523)	−1.523 (−1.523)	−6.477 (−6.477)

In parenthesis, the Yamaguchi values arising from Eq. (5). (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

Table 7. Values (in cm^{-1}) of the coupling constant J for the $H_4(T_d)$ cluster at stretched distances H—H (d/Å) and UHF and UB3LYP theory levels using STO-3G, 6–31G, 6–31G(d,p), and cc-pVTZ basis sets.

	UHF				UB3LYP			
d/Å	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ	STO-3G	6–31G	6–31G(d,p)	cc-pVTZ
2.0	−1686 (−1635)	−1486 (−1444)	−1470 (−1428)	−1446 (−1404)	−2733 (−2566)	−2401 (−2307)	−2372 (−2282)	−2266 (−2149)
2.2	−1001 (−978.9)	−1007 (−979.6)	−999.0 (−971.8)	−972.3 (−946.3)	−1800 (−1701)	−1865 (−1761)	−1846 (−1744)	−1793 (−1695)
2.4	−553.3 (−545.7)	−642.8 (−629.8)	−637.0 (−623.8)	−635.9 (−623.4)	−1096 (−1053)	−1334 (−1266)	−1326 (−1259)	−1305 (−1252)
2.6	−293.1 (−291.0)	−394.7 (−389.2)	−391.2 (−385.6)	−389.1 (−383.8)	−630.8 (−616.9)	−917.5 (−882.0)	−912.3 (−877.4)	−902.8 (−878.3)
2.8	−147.5 (−146.9)	−235.0 (−232.8)	−232.7 (−230.6)	−231.3 (−229.4)	−351.4 (−347.4)	−611.0 (−598.9)	−607.0 (−591.4)	−608.4 (−598.4)
3.0	−71.56 (−71.44)	−136.7 (−135.9)	−135.1 (−134.3)	−134.0 (−133.3)	−191.8 (−190.7)	−396.2 (−389.7)	−393.8 (−387.5)	−403.1 (−399.1)
3.225	−30.26 (−30.24)	−71.52 (−71.30)	−70.90 (−70.68)	−70.29 (−70.08)	−95.99 (−95.74)	−238.3 (−236.2)	−235.0 (−232.8)	−252.8 (−251.4)
3.5	−11.46 (−11.46)	−30.80 (−30.77)	−31.08 (−31.05)	−32.05 (−32.01)	−41.36 (−41.33)	−120.6 (−120.2)	−119.5 (−119.2)	−143.4 (−143.0)
4.0	−1.149 (−1.149)	−5.685 (−5.685)	−5.686 (−5.686)	−6.559 (−6.555)	−9.069 (−9.068)	−31.67 (−31.65)	−30.75 (−30.74)	−51.73 (−51.70)
5.0	−0.010 (−0.010)	−0.086 (−0.086)	−0.084 (−0.084)	−0.248 (−0.248)	−0.435 (−0.435)	−1.590 (−1.590)	−1.490 (−1.490)	−5.991 (−5.991)

In parenthesis, the Yamaguchi values arising from Eq. (5). (1 cm^{-1} = 4.556 microhartrees = 2.859 cal/mol)

their performance, in terms of the transferability, is very similar at both levels of theory.

In Tables 5, 6, and 7, we have gathered coupling constant values J_{HH} for the systems $H_2(D_{\infty h})$, $H_3(D_{3h})$, and $H_4(T_d)$, respectively. These Tables contain results arising from the Yamaguchi approach and those from our own algorithms to make a suitable comparison between both procedures. We have chosen these systems for simplicity as they possess a unique value for their coupling constants and a unique distance between any nucleus pair. Consequently, the Yamaguchi treatment can be formulated by Eq. (5); alternatively our results have been obtained from the values of two-center local spins $<\hat{S}^2>_{AB}$ [Eq. (7)] provided by the direct partitioning of the $<\hat{S}^2>$ quantity [Eq. (6)]. The comparison of these results has been performed using identical computational conditions (correlation level and basis set). As can be seen from these tables, the magnitude of the coupling constants obtained from both methods turns out to be very similar, and it is almost coincident around 3 Å (the internuclear distance to which the results become transferable). The dependence of these results on the level of electronic correlation of the wave function and the basis sets utilized is also quite similar for both procedures. To get a clearer insight into the basis set effects on the J values, we have performed all these calculations using four basis sets, the minimum STO-3G basis and the extended 6–31G, 6–31(d,p), and cc-pVTZ ones. As can be observed in these Tables, in all cases there are big differences between the J values obtained using the STO-3G basis and the corresponding values on 6–31G, 6–31G(d,p), and cc-pVTZ bases, which are fairly similar. These results point out that convergence can be obtained with sufficiently large basis sets. These findings are in agreement with previous studies involving different approaches to determine coupling constants[28] and spin populations.[35]

Concluding Remarks

In this work, we have studied the ability of using two-center local spin values to evaluate coupling constants within the Heisenberg spin Hamiltonian model. The two-center local spins utilized to perform this task have been those arising from a direct partitioning of the $<\hat{S}^2>$ quantity corresponding to an N-electron system. Our proposals have been applied to describe coupling constants in several Hydrogen clusters, with

different geometrical arrangements, and in the HeH_2 aggregate, in a wide range of internuclear distances beyond the bonding regions. The results show that the regions in which the coupling constant J_{HH} is transferable from the H_2 molecule to larger clusters are similar to those obtained from more sophisticated methods. Our procedure is conceptually simple and computationally suitable; its dependence on the level of correlation of the wave functions and the basis sets is similar to that exhibited by other exact or approximated approaches. We are currently working on the application of this methodology to describe architectures of heteroborane compounds and carborane clusters to determine their magnetic properties.

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Keywords: Heisenberg spin Hamiltonian · coupling constants · spin populations

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