

# Relationship between H–D Spin–Spin Coupling and Internuclear Distance in Molecular Hydrogen Complexes

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**Abstract:** An essentially identical linear relationship between the spin–spin coupling constant  $J_{\text{HD}}$  and internuclear separation  $r_{\text{HH}}$  in closed-shell “eighteen electron”  $\eta^2\text{-H}_2$  molecular hydrogen complexes is both predicted by quantum chemical calculations for complexes of the type  $[\text{Os}(\text{II})(\text{NH}_3)_4\text{L}^z(\eta^2\text{-H}_2)]^{(z+2)+}$  for a wide range of *trans* ligands L and found experimentally for a series of complexes of Fe, Cr, Ru, and Os, also containing a variety of ligands. Simple electronic structural considerations are proposed in order to provide a preliminary interpretation of these remarkable results.

The measurement and interpretation of hydrogen–deuterium coupling constants ( $J_{\text{HD}}$ ) have played an important role in the structural characterization of many transition-metal dihydrogen complexes. It has recently been shown<sup>1a</sup> that, at least for  $\eta^2\text{-H}_2$  complexes of Osmium of the type  $[\text{Os}(\text{NH}_3)_4\text{L}^z(\eta^2\text{-H}_2)]^{(z+2)+}$  (type **1**), where  $\text{L}^z$  is a *trans* ligand of charge  $z$ , it is possible to calculate  $J_{\text{HD}}$  to reasonable accuracy using density functional theory (DFT). The method which appears to account most successfully for correlation effects in these systems<sup>1</sup> is use of the BLYP functional, which utilizes the Becke gradient corrected exchange functional<sup>2</sup> and the Lee, Yang, and Parr correlation functional;<sup>3</sup> this method is implemented in the GAUSSIAN 94 software package.<sup>4</sup> These are the first DFT calculations of this quantity for molecular hydrogen complexes. It should be noted that the recent work of Malkin *et al.*<sup>5,6</sup> on a range of small organic molecules has shown that DFT is capable of providing an accurate description of spin–spin coupling, and thus there is considerable promise for the calculation of coupling constants in a wide range of molecules. The relation of  $J_{\text{HD}}$  to other properties of complexes of type **1** was also investigated: one such was the theoretical relationship between  $J_{\text{HD}}$  and the internuclear separation  $r_{\text{HH}}$ . Over the range of  $J_{\text{HD}}$  studied (5–23 Hz), a linear relationship was found, and can be expressed as:

$$r_{\text{HH}} = 1.38 - 0.0187J_{\text{HD}} \pm 0.02 \text{ \AA} \quad (1)$$

where  $J_{\text{HD}}$  is in hertz and  $r_{\text{HH}}$  in angstroms.

There has also for some time been experimental evidence for a linear relationship between  $J_{\text{HD}}$  and  $r_{\text{HH}}$  in a wide variety

of  $\eta^2\text{-H}_2$  complexes.<sup>7–9</sup> The values of internuclear distance used in this context have come from several sources—direct measurement in the solid state by X-ray or neutron diffraction, or indirectly from solid-state or solution NMR measurements. The most recent comparison<sup>10</sup> includes 15 molecules for which  $r_{\text{HH}}$  has been obtained in the solid state. It is found that a linear relationship with  $J_{\text{HD}}$  measured in solution holds over the range 7–35 Hz of  $J_{\text{HD}}$ , expressible as:

$$r_{\text{HH}} = 1.42 - 0.0167J_{\text{HD}} \pm 0.04 \text{ \AA} \quad (2)$$

This correlation comprises closed-shell 18-electron complexes of Fe, Cr, Ru, and Os, with a wide variety of ligands. It may be thought remarkable that it should be so similar to that of eq 1 found theoretically for Os compounds of type **1**—and indeed that an essentially single relationship should pertain for such an extensive range of chemical structures.

While detailed calculation is required to explore these relationships in depth, some preliminary insight into their origin can be obtained in a simple manner. We note firstly that there is good reason to believe that the bonding of  $\text{H}_2$  to the metal in  $\eta^2\text{-H}_2$  complexes is in all cases of the same general type, resulting essentially from partial transfer of charge from the filled  $\sigma$  orbital of  $\text{H}_2$  to an empty  $d\sigma$  orbital of the metal, accompanied by back-transfer from a filled metal  $d\pi$  orbital to the antibonding (virtual)  $\sigma^*\text{H}_2$  orbital. Calculations at the MP2 level of *ab initio* theory<sup>11</sup> have shown that in representative cases this is an excellent description of the charge flow accompanying binding of  $\text{H}_2$ .

In the simplest description, the free  $\text{H}_2$  bonding and virtual orbitals are linear combinations of 1s functions  $\phi_a, \phi_b$  centered

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on nuclei a and b, i.e.

$$\begin{aligned}\sigma &= (2(1+S))^{-1/2}(\phi_a + \phi_b) = c_1(\phi_a + \phi_b) \\ \sigma^* &= (2(1-S))^{-1/2}(\phi_a - \phi_b) = c_2(\phi_a - \phi_b)\end{aligned}\quad (3)$$

where  $S$  is the orbital overlap.

The essential features of the bonding of  $H_2$  can be expressed in terms of these orbitals and the metal  $d\sigma$  and  $d\pi$  orbitals with which they are respectively coupled. We thus write, assuming for simplicity orthogonality of metal and hydrogen atomic functions,

$$\begin{aligned}\psi_1 &= \alpha\sigma + (1 - \alpha^2)^{1/2}d_\sigma \\ \psi_2 &= \beta\sigma^* + (1 - \beta^2)^{1/2}d_\pi \\ \psi_3 &= (1 - \alpha^2)^{1/2}\sigma - \alpha d_\sigma \\ \psi_4 &= (1 - \beta^2)^{1/2}\sigma^* - \beta d_\pi\end{aligned}\quad (4)$$

with  $0.5 \leq \alpha^2 \leq 1$  and  $0 \leq \beta^2 \leq 0.5$ . In the ground state of the complex, orbitals  $\psi_1$  and  $\psi_2$  are doubly occupied.

It is useful to introduce the concept of bond index. The bond index  $P_{AB}$  between atoms A and B is defined as (see refs 12 and 13 and references therein):

$$P_{AB} = \sum_{\mu_A} \sum_{\lambda_B} (\mathbf{PS})_{\mu_A \lambda_B} (\mathbf{PS})_{\lambda_B \mu_A} \quad (5)$$

where  $\mu_A$  and  $\lambda_B$  represent atomic orbitals localized on atoms A and B, respectively.

The bond index  $P_{HH}$  will thus be a function of the 1s orbital structure: in terms of the above molecular functions, we have for the ground state for the H–H bond index

$$P_{HH}^{1/2} = \alpha^2 - \beta^2 \quad (6)$$

so that the H–H bond can be considered weakened by either  $\sigma$ -donation to the metal (which reduces  $\alpha$ ) or  $\pi$ -back-donation from the metal (which increases  $\beta$ ), or a combination of both, in accordance with the qualitative description mentioned earlier.

A reduced (dimensionless) spin–spin coupling constant  $J_{HD}$  can be defined as  $J_{HD}/J_{HD}^0$ , where  $J_{HD}^0$  is the value for the free molecule at the equilibrium separation. There is clearly a close connection between  $J_{HD}$  and bond index: both lie in the range 0–1, with  $J_{HD} = 1$  when  $P_{HH} = 1$  and likewise  $J_{HD} = 0$  when  $P_{HH} = 0$ . In fact, calculations at the SCF/MP2 *ab initio* level<sup>11</sup> for systems of type **1** indicate an approximately linear relationship, but the values of  $J_{HD}$  obtained by this method are not sufficiently accurate to establish the precise nature of the dependence. Some insight can be obtained from examination of the perturbation theory expression for  $J_{HD}$  (e.g. ref 14), i.e.

$$J_{AB} = -\Lambda_{AB} \sum_a \sum_i ({}^3\Delta E_{i \rightarrow a})^{-1} \langle \psi_i | \delta(r_A) | \psi_a \rangle \langle \psi_a | \delta(r_B) | \psi_i \rangle \quad (7)$$

where

$$\Lambda_{AB} = (1/\pi^2)(2/3\mu_o g_s \mu_B)^2 \gamma_A \gamma_B \quad (8)$$

In these expressions,  ${}^3\Delta E_{i \rightarrow a}$  is the energy of excitation from

occupied levels  $\{\psi_i\}$  to virtual levels  $\{\psi_a\}$  (triplet configuration) and  $r_A$  is the position coordinate of an electron relative to nucleus A. In SI units,  $\mu_o$  is the permittivity of free space,  $g_e$  is the free electron  $g$ -value,  $\mu_B$  is the Bohr magneton, and  $\gamma_A$  and  $\gamma_B$  are the respective gyromagnetic ratios.

This expression is further simplified if, as suggested by Santry and Pople,<sup>14</sup> we use the independent orbital approximation and set the excitation energy  ${}^3\Delta E_{i \rightarrow a}$  equal to the difference of orbital energies  $\epsilon_a - \epsilon_i$ . In a very simple illustrative example, we set the off-diagonal energy integrals equal to unity, and taking these as the energy unit, set  $\epsilon(d_\pi)$  and  $\epsilon(d_\sigma)$  equal to  $\pm\Delta$ , respectively, symmetrically displaced around the energy of the H(1s) orbital. From the approximation to eq 7, using the orbitals in (4) with  $S = 0$ , over the range  $0.5 \leq \Delta \leq 2$ ,  $J_{HD}$  is equal to  $P_{HH}$  within ca. 10%. This of course serves only as an illustration of the way in which such a relationship can originate; but, anticipating further calculations at the DFT level, we propose that in fact for the systems considered,

$$J_{HD} = P_{HH} \quad (9)$$

Thus on this model the reduced spin–spin coupling constant is a direct measure of the H–H bond index. This is unity for the free molecule, and zero for the dissociated classical dihydride.

The next question is the relationship of  $P_{HH}$  to the internuclear separation  $r_{HH}$ . Calculations at the SCF/MP2 level of theory<sup>11</sup> indicate that this is essentially linear. Defining a reduced internuclear separation  $r'_{HH}$  as  $r'_{HH} = r_{HH}/r_{HH}^0$ , where  $r_{HH}^0$  is the free molecule equilibrium separation, this relationship can be written generally as

$$r'_{HH} = a + bP_{HH} \quad (10)$$

The SCF/MP2 calculations<sup>1</sup> suggest values of  $a$  and  $b$  as very approximately of the order of  $2 \pm 0.4$  and  $-1.3 \pm 0.3$ , respectively. However, these calculations are believed to seriously underestimate the spread of  $r_{HH}$  in systems of type **1**; while there is evidently an essentially linear relationship, there is uncertainty about its exact nature from these calculations. Again anticipating further calculations at the DFT level, we shall make the assumption that in fact this takes the very simple form

$$r'_{HH} = a - P_{HH} \quad (11)$$

Since  $P_{HH} = 1$  when  $r'_{HD} = 1$ , it follows that  $a = 2$ , i.e.,

$$r'_{HH} = 2 - P_{HH} \quad (12)$$

which leads to the correlation with  $J'_{HD}$ :

$$r'_{HH} = 2 - J'_{HD} \quad (13)$$

On this model, eq 13 encapsulates the relation between H–H internuclear separation and spin–spin coupling constant over the range of  $\eta^2$ - $H_2$  complexes. The H–H bond is thus considered “broken” when the internuclear distance is twice the free molecule equilibrium separation.

For comparison with the calculated and experimental relationships of eqs 1 and 2, we convert to physical units, taking  $r_{HH}^0 = 0.74 \text{ \AA}$  and  $J_{HD}^0 = 43.0 \text{ Hz}$ .<sup>15</sup> Equation 13 then becomes

$$r_{HH} = 1.48 - 0.017J_{HD} \text{ \AA} \quad (14)$$

with  $J_{HD}$  in hertz. This differs from the empirical correlation of eq 2 only by a small difference in the intercept (note that in Figure 5 of ref 10 the intercept is actually approximately 1.48

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Å: relationships proposed in refs 7–9 have similar gradients but somewhat variable intercepts). The H–H bond is considered “broken” at  $r_{\text{HH}} = \text{ca. } 1.5 \text{ \AA}$  and the gradient  $-0.017 \text{ \AA Hz}^{-1}$  is the ratio  $-r^{\circ}/J^{\circ} = -0.74/43$ . While further experiment and calculation may reveal departures from approximate linearity at small separations, and scatter is always to be expected owing to perturbations arising from details of the complex’s structure and solvent and temperature effects, the existence of a general correlation of the above type can evidently be rationalized in a simple fashion.

In the above we have attempted to provide some insight into the forms of eqs 1 and 2 by connecting the terms in them to the H–H bond index  $P_{\text{HH}}$ . The length and strength of this bond is determined by the strength of the interaction with the metal to which it is coupled, and an indication of how this is so is clearly necessary.

We note first that a property of the bond index is that the sum of the indices to a given atom is equal to that atom’s valency.<sup>12,13</sup> Since this is unity for H, the H–H and metal–H bond indices are complementary, i.e.

$$P_{\text{MH}} = 1 - P_{\text{HH}} \quad (15)$$

as shown for type **1** molecules in ref 11. As the H<sub>2</sub> molecule approaches the metal,  $P_{\text{HH}}$  drops from unity to its equilibrium value, and the M–H bond acquires a strength characterized by the index  $P_{\text{MH}}$ . The binding to the metal is the primary cause of the modulation of H–H distance, and eq 15 indicates this in a transparent way. According to the above analysis, the M–H bond index can be obtained from the reduced coupling constant, i.e.  $P_{\text{MH}} = 1 - J'_{\text{HD}}$ . Thus, for example, for the complex of type **1** with  $L^z = \text{H}_2\text{O}$ , calculated to be strongly bonded, the observed value<sup>16</sup> of  $J_{\text{HD}}$  of 8.1 Hz implies an H–H bond index  $P_{\text{HH}}$  of 0.19 and an Os–H bond index  $P_{\text{MH}}$  of 0.81. By contrast, the value of  $J_{\text{HD}}$  of 35 Hz reported for  $\text{Cr}(\text{H}_2)(\text{CO})_3(\text{P}^i\text{Pr}_3)_2$ <sup>17</sup> indicates an H–H bond index of 0.81, with a Cr–H bond index of 0.19, the reverse of the situation for the Os complex. (These M–H bond indices will be expected to have highly nonlinear relationships to the bond distances  $r_{\text{MH}}$ .) Although calculated bond indices are of course not independent of basis set choice, the use of the concept should serve as a useful qualitative guide to the chemical significance of the spin–spin coupling constant.

More fundamentally, we would seek to connect both  $J_{\text{HD}}$  and  $r_{\text{HH}}$  to further observable (at least in principle) quantities. The strength of the metal–H<sub>2</sub> bond is the measurable quantity of most basic interest characterizing molecular hydrogen compounds, and it, not only the bond index, should clearly be related to the regularities discussed above. No experimental information is yet available for the H<sub>2</sub> binding energy for most  $\eta^2\text{-H}_2$  systems. However, it is clear that correlations of the type shown in eqs 1 and 2 with binding energy require that the binding energy should vary with reduced H–H distance  $r'_{\text{HH}}$  and reduced coupling constant  $J'_{\text{HD}}$  with essentially identical gradients. The DFT calculations for molecules of type **1** can be used to test this. These indicate<sup>1</sup> that there are indeed at this level of

calculation linear correlations of both  $J_{\text{HD}}$  and  $r_{\text{HH}}$  with the H<sub>2</sub> binding energy  $-\Delta E(\text{H}_2)$ . For  $J_{\text{HD}}$  (Hz), this can be expressed as

$$J_{\text{HD}} = 43 + 0.79\Delta E(\text{H}_2) \quad (16)$$

or, in reduced units, with  $J^{\circ}_{\text{HD}} = 43.0 \text{ Hz}$ ,

$$J'_{\text{HD}} = 1.00 + 0.018\Delta E(\text{H}_2) \quad (17)$$

where  $\Delta E(\text{H}_2)$  is in  $\text{kcal mol}^{-1}$  in both expressions.

The correlation for  $r'_{\text{HH}}$  (with  $r^{\circ} = 0.74 \text{ \AA}$ ) is approximately

$$r'_{\text{HH}} = 0.81 - 0.019\Delta E(\text{H}_2) \quad (18)$$

and the combination of these results in the relationship of eq 1 between  $J_{\text{HD}}$  and  $r_{\text{HH}}$  discussed above to within the precision of these relations.

Thus, for systems of type **1**,  $-J'_{\text{HD}}$  and  $r'_{\text{HH}}$  are calculated to vary with metal–H<sub>2</sub> binding energy with essentially identical gradients. This is the necessary condition for a relationship of the type of eq 1 to hold, and may be regarded as its basic determinant. The similarity of the theoretical  $r_{\text{HH}}/J_{\text{HD}}$  correlation for type **1** systems to the experimental correlation for a wide range of systems (eq 2) suggests that this near-equality of dependence of  $-J_{\text{HD}}$  and H<sub>2</sub> internuclear separation on H<sub>2</sub> binding energy will be a general feature of closed-shell “18-electron”  $\eta^2\text{-H}_2$  complexes, although individual values of these gradients will not necessarily be identical with those for the type **1** Os systems. The extremely shallow nature of the H–H potential curve in these complexes, calculated at a number of different levels of *ab initio* theory,<sup>11,18</sup> might suggest sensitivity of the H–H separation to environmental effects which would complicate such relationships; however, there is as yet no evidence that these are of great importance.

The bond length dependence of spin–spin coupling in free H<sub>2</sub> is calculated<sup>1a,19</sup> to be very different, **increasing** to a maximum for all bound levels. Calculations for a typical molecule of type **1** with  $L = \text{Cl}^-$  (ref 1a) indicate that as hydrogen approaches the Os center, this positive gradient decreases to approximately zero at an Os–H separation of ca. 1 Å greater than the equilibrium value, and attains its final linear negative value at the equilibrium distance (1.63 Å). The possibly counter-intuitive behavior in the free molecule can be qualitatively attributed<sup>19</sup> to the magnetic perturbation becoming comparable with the energy gap between the ground state and lowest  $^3\Sigma_u^+$  state, to which it is coupled by the spin–spin interaction; in the  $\eta^2\text{-H}_2$  complexes, mixing with metal orbitals will ensure a larger energy gap and thus the negative gradient both calculated and observed at equilibrium.

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