

Nuclear spin-spin coupling in HD, HT, and DT

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(Dated: January 1, 2018)

The interaction between nuclear spins in a molecule is exceptionally sensitive to the physics beyond the Standard Model. However, all present calculations of the nuclear spin-spin coupling constant J are burdened by computational difficulties, which hinders the comparison to experimental results. Here, we present a variational approach and calculate the constant J in the hydrogen molecule with the controlled numerical precision, using the adiabatic approximation. The apparent discrepancy with experimental result is removed by an analysis of nonadiabatic effects based on the experimental values of the J -constant for HD, HT and DT molecules. This study significantly improves the reliability of the NMR theory for searching new physics in the spin-spin coupling.

PACS numbers:

Introduction. The line splitting observed in a nuclear magnetic resonance (NMR) experiment is one of the smallest splittings directly observed in molecular spectroscopy. It results from the indirect interaction between nuclear spins [1]. Typically, the magnitude of the nuclear spin-spin coupling constant J is many orders of magnitude smaller than the energy of the fundamental rotational excitation. The indirect spin-spin interaction of nuclei was discovered by Hahn and Maxwell [2] and independently by McNeil, Slichter, and Gutowsky [3] in 1951. In the HD molecule, the J -coupling (≈ 43 Hz) was first observed by Carr and Purcell [4]. The most accurate measurements, reported by Neronov *et al.* [5, 6] and recently by Garbacz *et al.* [7, 8], reach the accuracy of 0.01 Hz. Due to its extreme smallness, the J -coupling is potentially sensitive to the physics beyond the Standard Model (BSM). In particular, it could yield constraints on anomalous spin-dependent axion-nucleon interactions at the atomic scale [9], which are several orders of magnitude more stringent than those inferred from any other sources [10, 11].

In order to test the accuracy of NMR theory and to search for BSM physics, the high accuracy measurements must be put together with equally accurate theoretical predictions. In this paper we report on high-precision calculations of J in the adiabatic approximation, analyze nonadiabatic effects by comparison with experimental values for HD, HT, and DT molecules, and estimate the relativistic and QED corrections. Nonadiabatic effects, or more precisely, the finite nuclear mass corrections, in spite of their importance, have previously been completely omitted in all the works devoted to spin-spin coupling constant, including those of [9].

Several calculations of the leading contribution to the coupling constant J have been performed using methods based on the one-electron approximation and direct use of Ramsey's formulas [12–15]. This standard approach is widely implemented in quantum chemistry programs and applied to many molecular systems. However, all

the presently developed methods ignore the fact that the sum over intermediate states is only conditionally convergent and therefore the numerical accuracy is difficult to control. Here, we demonstrate an algebraic elimination of all the divergences. Transformed formulas lead to finite results for a definite symmetry of intermediate electronic states, and allow the variational approach to be employed for all the second-order contributions, which in turn ensures high numerical precision, in contrast to all the previous approaches. Finally, we perform numerical calculations for the hydrogen molecules using the explicitly correlated basis functions. The difference of the obtained results with the experimental values is explained in terms of the finite nuclear mass effects.

Physics of the J -coupling. The theory of the nuclear spin-spin interaction in a diatomic molecule was first formulated by Ramsey [1]. His formula for the interaction of nuclei A and B distant from each other by R , rewritten in our notation, is

$$J(R) \vec{I}_A \cdot \vec{I}_B = 2 \left\langle H_A \frac{1}{E(R) - H} H_B \right\rangle + \sum_a \frac{e^2}{m} \langle \vec{\mathcal{A}}(\vec{r}_{aA}) \cdot \vec{\mathcal{A}}(\vec{r}_{aB}) \rangle, \quad (1)$$

where the molecule is described by the clamped-nuclei Hamiltonian

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V \quad (2)$$

with (α is the fine structure constant)

$$V = -\frac{\alpha}{r_{1A}} - \frac{\alpha}{r_{1B}} - \frac{\alpha}{r_{2A}} - \frac{\alpha}{r_{2B}} + \frac{\alpha}{r_{12}} + \frac{\alpha}{R}, \quad (3)$$

and energy $E(R)$. The interaction of the spin of nucleus $X (= A, B)$ with electrons is

$$H_X = \sum_a \frac{\alpha g_X}{m M_X} \left(\frac{2}{3} g \vec{s}_a \cdot \vec{I}_X \pi \delta(\vec{r}_{aX}) + \frac{1}{2} \vec{I}_X \cdot \frac{\vec{r}_{aX}}{r_{aX}^3} \times \vec{p}_a + \frac{3}{4} g s_a^i I_X^j \frac{r_{aX}^i r_{aX}^j - \frac{1}{3} r_{aX}^2 \delta^{ij}}{r_{aX}^5} \right) \quad (4)$$

and the vector potential $\vec{\mathcal{A}}$ due to the nuclear magnetic moment is

$$e \vec{\mathcal{A}}(\vec{r}_{aX}) = -\frac{\alpha g_X}{2 M_X} \vec{I}_X \times \frac{\vec{r}_{aX}}{r_{aX}^3}. \quad (5)$$

The electron and nucleus g -factors, g and g_X , the mass ratios, and the other physical constants, are known to high accuracy. So, in principle, the J -coupling can be calculated to high accuracy too. However, Ramsey's formula has several limitations. In particular, it does not account for relativistic nor QED effects and to the best of our knowledge nobody so far has described these effects in a complete manner. More importantly, the lack of the relativistic correction is responsible for the exponential growth of $J(R) \sim \exp(2R)$, so Ramsey's formula loses its validity at large R . Another limitation of this formula is the neglect of the finite nuclear masses and we shall discuss this issue later on.

The total spin-spin coupling J is conventionally split into four parts, namely the Fermi contact (FC), paramagnetic spin-orbit (PSO), spin-dipole (SD), and diamagnetic spin-orbit (DSO)

$$J = J_{\text{FC}} + J_{\text{SD}} + J_{\text{PSO}} + J_{\text{DSO}}. \quad (6)$$

Since the electronic wave function for the hydrogen molecule is a product of a spatial and spin singlet functions, all the electron spin operators can be replaced by their difference, namely $\vec{s}_1 \rightarrow (\vec{s}_1 - \vec{s}_2)/2$. Next, using the identity $\langle (s_1 - s_2)^i (s_1 - s_2)^j \rangle = \delta^{ij}$ and $\kappa = m \alpha^6 g_A g_B m^2 / (M_A M_B)$, these parts can be expressed as

$$J_{\text{FC}} = \frac{g^2 \kappa}{72} \left\langle Q_1(A) \frac{1}{E - H} Q_1(B) \right\rangle \quad (7)$$

$$J_{\text{PSO}} = \frac{\kappa}{6} \left\langle \vec{Q}_2(A) \frac{1}{E - H} \vec{Q}_2(B) \right\rangle \quad (8)$$

$$J_{\text{SD}} = \frac{3g^2 \kappa}{32} \left\langle Q_3^{ij}(A) \frac{1}{E - H} Q_3^{ij}(B) \right\rangle \quad (9)$$

$$J_{\text{DSO}} = \frac{\kappa}{6} \left\langle \frac{\vec{r}_{1A} \vec{r}_{1B}}{r_{1A}^3 r_{1B}^3} + \frac{\vec{r}_{2A} \vec{r}_{2B}}{r_{2A}^3 r_{2B}^3} \right\rangle, \quad (10)$$

where

$$Q_1(A) = 4\pi [\delta^3(r_{1A}) - \delta^3(r_{2A})] \quad (11)$$

$$\vec{Q}_2(A) = \frac{\vec{r}_{1A}}{r_{1A}^3} \times \vec{p}_1 + \frac{\vec{r}_{2A}}{r_{2A}^3} \times \vec{p}_2 \quad (12)$$

$$Q_3^{ij}(A) = \frac{r_{1A}^{ij}}{r_{1A}^5} - \frac{r_{2A}^{ij}}{r_{2A}^5} \quad (13)$$

and where $r^{ij} \equiv r^i r^j - \frac{\delta^{ij}}{3} r^2$.

Conditional convergence. There is at least one subtle point in the numerical evaluation of these second-order matrix elements. The resolvent $1/(E - H)$ is conventionally replaced with a sum over states or pseudostates

expressed in terms of some basis functions. This sum is only conditionally convergent. For example, the separate sums over gerade and ungerade states for HD molecule are divergent. It is because the exact perturbed wave function $\phi = (E - H)^{-1} Q_1(B) \phi$ behaves as $\sim 1/r_{1B}$ for small distances from nucleus B . Now, if we impose the gerade or ungerade symmetry, the perturbed wave function contains $1/r_{1B} \pm 1/r_{1A}$. It becomes an ill defined expression, when multiplied by the Dirac $\delta(r_{1A})$ from $Q_1(A)$, which appears as the divergence of the separate sums over gerade or ungerade pseudostates. So, if the sum over intermediate states is only conditionally convergent, the second-order matrix elements of Eqs. (7)–(9) may give an arbitrary value. For this reason, we transform the second-order matrix elements to a more regular form, which provides several advantages over the original one. First of all, the regularized individual parts take finite values, which removes the problem of cancellation of infinities. Second, the regularization enables symmetric second-order quantities with well-defined lower bound to be formed, which gives the opportunity to employ variational principle and optimize the nonlinear parameters for each individual matrix element. Finally, the regularized matrix elements exhibit significantly faster convergence with the growing size of the basis. All together, these three features allow highly accurate results to be obtained even with relatively small basis sets.

Regularization. The regularization procedure goes as follows [16]. Let Q be an operator to be regularized. We can assume that it depends only on one electron variables $Q = Q(\vec{r}_1)$. In all the considered cases one can find an operator \tilde{Q} such that $-\nabla_1^2 \tilde{Q} \equiv -[\nabla_1, [\nabla_1, \tilde{Q}]] = Q$, so

$$Q = -(\nabla_1^2 + \nabla_2^2) \tilde{Q} = [Q]_r - 2 \{E - H, \tilde{Q}\}, \quad (14)$$

where

$$[Q]_r = 4(E - V) \tilde{Q} - 2 \vec{p}_1 \tilde{Q} \vec{p}_1 - 2 \vec{p}_2 \tilde{Q} \vec{p}_2. \quad (15)$$

The second-order matrix elements are regularized following the identity

$$\left\langle Q(A) \frac{1}{E - H} Q(B) \right\rangle = \left\langle [Q(A)]_r \frac{1}{E - H} [Q(B)]_r \right\rangle + 2 \langle Q' \rangle, \quad (16)$$

where

$$Q' = (\nabla_1^2 + \nabla_2^2) (\tilde{Q}(A) \tilde{Q}(B)) - \vec{\nabla}_1(\tilde{Q}(A)) \vec{\nabla}_1(\tilde{Q}(B)) + \vec{\nabla}_2(\tilde{Q}(A)) \vec{\nabla}_2(\tilde{Q}(B)). \quad (17)$$

The FC-part is regularized with

$$\tilde{Q}_1(A) = \frac{1}{r_{1A}} - \frac{1}{r_{2A}}, \quad (18)$$

the PSO-part remains unchanged, and the SD-part is regularized with

$$\tilde{Q}_3^{ij}(A) = \frac{1}{6} \left(\frac{r_{1A}^{ij}}{r_{1A}^3} - \frac{r_{2A}^{ij}}{r_{2A}^3} \right). \quad (19)$$

Finally, the first-order terms Q' are further regularized, using Eq. (14), to reduce their singularities and improve convergence of matrix elements.

Numerical results. The variational wave function for the electronic ground state,

$$\psi(^1\Sigma_g^+) = \sum_i c_i \psi_i(\vec{r}_1, \vec{r}_2), \quad (20)$$

$$\psi_i = (1 + \hat{i})(1 + P_{1\leftrightarrow 2})\phi_i(\vec{r}_1, \vec{r}_2), \quad (21)$$

where \hat{i} and $P_{1\leftrightarrow 2}$ are the inversion and the electron exchange operators, can be accurately represented in the basis of explicitly correlated Gaussian (ECG) functions of the form

$$\phi = e^{-a_{1A} r_{1A}^2 - a_{1B} r_{1B}^2 - a_{2A} r_{2A}^2 - a_{2B} r_{2B}^2 - a_{12} r^2}. \quad (22)$$

The nonlinear a -parameters are determined variationally for every ECG basis function whereas the linear c -parameters are obtained from the solution of the generalized eigenvalue problem. The primary advantage of the ECG type of functions is that all integrals necessary for the calculations of nonrelativistic and relativistic operators can be evaluated efficiently as described in [17].

The regularized second-order matrix elements are split into twelve parts with definite symmetry and the definite electronic angular momentum $\vec{n} \cdot \vec{L}$, where $\vec{n} = \vec{R}/R$. These intermediate states are $^3\Sigma^+$, $^1\Sigma^-$, $^1\Pi$, $^3\Pi$, $^3\Delta$ with definite g or u symmetry. Each state is represented by 128-, 256-, and 512-term ECG functions with nonlinear a -parameters obtained by optimization of a pertinent second-order matrix element with the symmetrized operator $[Q(A) \pm Q(B)]_r$. Careful optimization at different basis length is crucial for maintaining good control of numerical precision.

TABLE I: Results of the extrapolation to a complete basis set limit and the comparison with previous calculations for individual contributions to J (in Hz) for HD at $R_e = 1.4$ au. Analogous results for HT and DT can be obtained by rescaling the HD results with pertinent ratios of nuclear magnetic moments. Physical constants taken from [18].

Basis set size	J_{FC}	J_{PSO}	J_{SD}	J_{DSO}	J
128	40.175 433	0.837 338 5	0.443 388	-0.314 225 8	41.142 234
256	40.174 626	0.836 695 0	0.442 969	-0.314 231 1	41.140 059
512	40.174 148	0.836 668 3	0.442 731	-0.314 231 4	41.139 316
∞	40.174 1(3)	0.836 665(15)	0.442 70(12)	-0.314 23	41.139 2(3)
References					
MCSCF [19]	40.186	0.818	0.438	-0.307	41.135
SOPPA(CCSD) [20]	40.19	0.76	0.50	-0.29	41.17
FCI [7]	40.185 7	0.836 0	0.448 6	-0.314 1	41.156 3

The numerical convergence with the progressing basis length for J_{FC} , J_{PSO} , J_{SD} , and J_{DSO} parts at the equilibrium distance $R = 1.4$ au is presented in Table I. The extrapolated numerical result for the total value of J is in agreement with previously published results but is considerably more accurate. This is due to the separate optimization of gerade and ungerade basis, which was possible only after the regularization of the second-order matrix elements.

$J(R)$ is a fast growing function of the internuclear distance R . For small R it may behave as $\sim R^{-1}$ or $\sim R^0$, but we have not been able to resolve between these two asymptotics. For large R , the $J(R)$ goes like $\sim R^{-5/2} \exp(2R)$, which corresponds to the large- R

asymptotic of the exchange energy [21]. This exponential growth is unphysical and is due to the neglect of relativistic corrections. The dependence of $J(R)$ multiplied by $R \exp(-2R)$ is presented in Fig. 1.

Despite the fact that the $J(R)$ curve flattens near the equilibrium distance, the temperature effect is non-negligible. Several of the lowest rotational states were included in the Boltzmann formula to obtain the spin-spin coupling constant corresponding to 300 K. For the rotational averaging we employed the Born-Oppenheimer interaction potential [23] augmented by the adiabatic corrections of [24], both obtained from highly accurate calculations with the James-Coolidge functions. Table II presents averaged results for temperatures of 0, 40, and

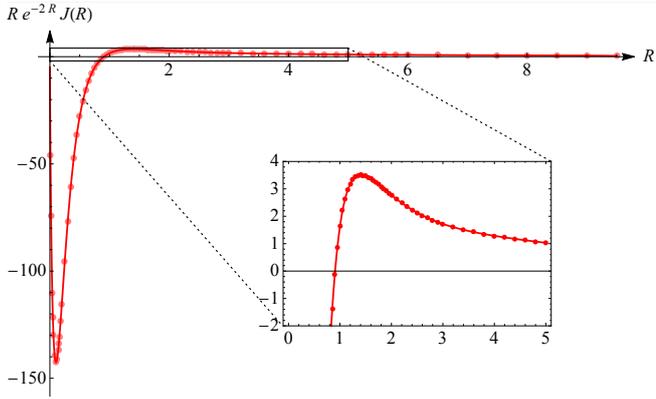


FIG. 1: Nuclear spin-spin interaction $J(R)$ times $R \exp(-2R)$ in Hz as a function of internuclear distance R in au, the equilibrium distance is near 1.4 au.

300 K with the comparison to experimental results. Most importantly, we observe a -0.19 Hz difference between the experiments and our calculation for the HD molecule. For HT and DT this difference amounts to -1.06 and -0.09 Hz, respectively. We note, that our results are obtained using adiabatic approximation and the theoretical uncertainty does not include effects due to the finite nuclear mass of the order of $O(m/\mu_n)$. These effects, not yet considered in the literature, are responsible for the above mentioned differences. One partially includes

TABLE II: Theoretical predictions in adiabatic approximation at $T = 300K$ compared to experimental value. The difference is interpreted as a finite nuclear mass correction of order $O(m_e/\mu_n)$. Results for $T = 40K$ are from [9] and our theoretical predictions are presented for the comparison with that work. Theoretical uncertainties are purely numerical, thus do not include those due to nonadiabatic, relativistic and QED corrections.

	Ref.	HD	HT	DT
$J_{\text{BO}}(R_e)$		41.139 2(3)	285.857(2)	43.880 7(3)
$\delta J(0K)$		1.968 0(9)	12.869(6)	1.554 6(7)
$\delta J(300K)$		0.199 5	1.391 8	0.215 3
$J(300K)$		43.306 7(9)	300.117(6)	45.650 6(9)
$J_{\text{exp}}(300K)$	[8]	43.12(1)	299.06(36)	45.56(2)
	[5, 6]	43.115(9)		
	[22]	43.130(15)		
$\delta J(40K)$		0.010 0		
$J(40K)$		43.117 2(9)		
$J_{\text{exp}}(40K)$	[9, 22]	42.94(4)		

them through the averaging of $J(R)$ with the nuclear vibrational function $\chi(R)$

$$J = \int d^3R J(R) \chi^*(R) \chi(R), \quad (23)$$

nevertheless, the neglected effects are of the order of the

ratio of the electron mass to the reduced nuclear mass m/μ_n , which e.g. for HD molecule is about $0.8 \cdot 10^{-3}$. Therefore, the use of Ramsey's formula alone limits the accuracy of J by at least $m/\mu_n J = 0.036$ Hz. To obtain a more reliable estimation, we replace the electron mass by the reduced one $\mu = m \mu_n / (m + \mu_n)$ in Ramsey's formula. Then, each Dirac δ in Eq. (7) scales as $(\mu/m)^3$, the nonrelativistic Hamiltonian in the denominator scales as μ/m , and the total factor in the dominating J_{FC} term is $(\mu/m)^5$. After expansion in the electron mass the finite nuclear mass correction becomes $-5 m/\mu_n J = -0.18$ Hz, which is close to the difference with the experiment of -0.19 Hz. Analogous estimation for HT and DT yields -1.09 and -0.10 Hz in comparison with discrepancy between experiment and theory equal to -1.12 and -0.09 Hz.

From the other side, the finite nuclear mass effects can be inferred from experimental values for different isotopes [8] as follows. Let us subtract from the experimental values $J_{\text{exp}}(300K)$ the theoretical predictions $J(300K)$ and rescale the remainder by magnetic moments of nuclei to that of HD. Such normalized remainders $\delta\tilde{J}$, differ due to different value of the reduced nuclear mass, as shown on Fig. 2. This dependence agrees with the expected be-

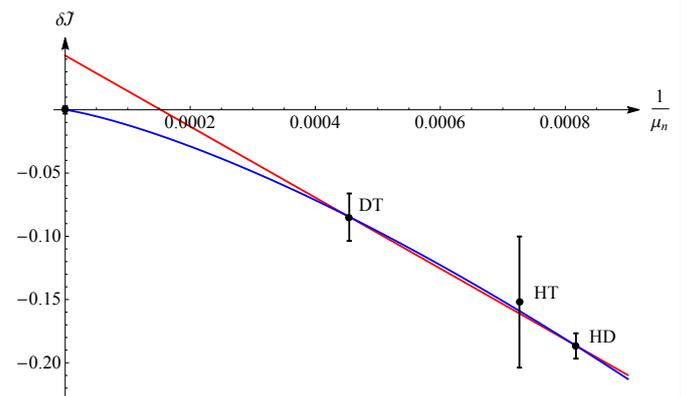


FIG. 2: The rescaled remainder of the nuclear spin-spin interaction $\delta\tilde{J}$ in Hz as a function of the reduced nuclear mass. The fitted curve (in blue) is of the form $A/\mu_n + B/\mu_n^{3/2}$, while the linear fit (in red) is $J_0 + C/\mu_n$, with $J_0 = 0.043$ Hz

havior of $\sim 1/\mu_n$, which is demonstrated by the fitted functions. We do not aim to analyze in details different fits because of large experimental uncertainties, but we claim that the finite nuclear mass effects account for the difference between theoretical predictions and experimental results, and should be precisely calculated prior looking for BSM physics in the spin-spin coupling [9]. These very challenging calculations can be performed using the nonadiabatic perturbation theory [25], or by using the fully nonadiabatic approach with explicitly correlated Gaussian or exponential functions. In both cases,

one should include additional electron-nucleus interactions not accounted for in Ramsey's formula.

Regarding other possible sources of theoretical uncertainties, the relativistic correction for the HD molecule at the equilibrium distance has been estimated numerically by Helgaker et al. [7] as being of the order of 0.01 Hz. Our estimation of this correction is $3\alpha^2 J_{\text{FC}} \approx 0.006$ Hz, which is twice the relativistic (so called Breit) correction to the hyperfine splitting in atomic hydrogen. Moreover, the radiative correction to J , again from the hydrogenic hyperfine splitting is $2(\ln 2 - \frac{5}{2})\alpha^2 J_{\text{FC}} = -0.0077$ Hz. Both corrections, regardless of the fact that they compensate each other to a large extent, are negligible at present.

Summary. The main results of this work are the development of a new computational method for the spin-spin coupling constant J including algebraic elimination of all singularities, the highly precise calculation for HD, HT, and DT molecules, and the resolution of the observed difference with experimental results in terms of finite nuclear mass effects. We established a benchmark, which is a reliable starting point for accurate evaluation of finite nuclear mass, relativistic, and QED corrections. Moreover, we notice, that the proposed regularization and variational optimization of the basis functions can be applied to other molecules enabling high-precision numerical results and the possibility to search for BSM physics in heavier systems, where it is significantly enhanced.

We wish to thank Michał Jaszuński for helpful comments to the manuscript. This work was supported by the National Science Center (Poland) Grant No. 2016/23/B/ST4/01821 and by PL-Grid Infrastructure.

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