

### Configuration-interaction and Hylleraas configuration-interaction methods in valence-bond theory: Calculation of the nuclear shielding constant for the ground state of the hydrogen molecule

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Values of the magnetic shielding constant in the ground state of the hydrogen molecule are calculated using explicitly correlated Gaussian functions. The total shielding at equilibrium amounts to 26.73 ppm.

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The most accurate calculations of two-electron two-center systems such as  $H_2$  have been performed with the Kołos-Wolniewicz wave function. In addition to the best potential-energy curves (see Refs. [1,2] and references therein), a wide range of very accurate expectation values [3,4] and electric and magnetic linear-response properties [2,5] have been calculated. However, computational difficulties arising from the evaluation of integrals containing  $r^{-3}$  type operators have been a serious obstacle to calculating such interesting molecular properties as nuclear magnetic shielding, spin-orbit coupling, electric field, etc. So far, for the elliptic coordinate basis set of the Kołos-Wolniewicz wave function, the required integral formulas have not been obtained, except for the electric-field gradient operator [6]. Another type of function, containing explicitly the interelectronic distance  $r_{12}$ , has been used for many years. In this method, which is a special case of the Hylleraas configuration-interaction (HCI) approach, the basis consists of Gaussian functions multiplied by either an exponential,  $\exp(-\gamma r_{12}^2)$ , or a linear,  $r_{12}$  correlation factor. Both these types of Gaussian basis sets have been tested for two-electron systems and give energies [7] comparable to those obtained using the Kołos-Wolniewicz function. Recently, we have proposed a HCI two-electron wave function of the valence-bond type (HCIVB) [8]:

$$\Psi_{\text{HCIVB}}(1,2) = \sum_i c_i F_i(1,2) r_{12}^{v_i}, \quad v_i = 0 \text{ or } 1, \quad (1)$$

where  $F_i$  are geminal functions defined as symmetrized products of primitive Cartesian Gaussian functions centered on the nuclei. For two-electron systems this wave function gives energies within  $1 \text{ cm}^{-1}$  of the best theoretical results. The aim of this paper is to demonstrate the ability of the HCIVB function to reproduce magnetic properties and to obtain accurate values of the magnetic shielding constant  $\sigma$  and the magnetizability  $\chi$  of  $H_2$ . This is the first calculation of  $\sigma$  with explicitly correlated wave functions. Throughout this article atomic units are used.

For a closed-shell molecule placed in a static uniform magnetic field  $\mathbf{B}$  and containing a nucleus  $N$  with a magnetic moment  $\mu_N$ , the electronic Hamiltonian may be written

$$\mathcal{H}(\mathbf{B}, \mu_N) = \frac{1}{2} \sum_k (-i \nabla_k + \mathbf{A}_k)^2 + V, \quad (2)$$

where  $V$  includes all Coulomb interactions, and  $\mathbf{A}_k$  is the vector potential describing the total magnetic field at the position of electron  $k$

$$\mathbf{A}_k = \frac{1}{2} \mathbf{B} \times \mathbf{r}_{kG} + \frac{1}{c^2} \frac{\mu_N \times \mathbf{r}_{kN}}{r_{kN}^3}. \quad (3)$$

In the above equations the symbols  $i$ ,  $\nabla$ , and  $c = 137.0359895$  have their usual meaning.  $\mathbf{r}_{kG}$  is the vector from a chosen gauge origin  $G$  to electron  $k$ , while  $\mathbf{r}_{kN}$  is the position of the  $k$ th electron with respect to the given nucleus  $N$ . Multiple perturbation theory applied to the Hamiltonian (2) and the assumption of the Coulomb gauge for the vector potential ( $\nabla \cdot \mathbf{A} = 0$ ) lead to the desired expressions for the diamagnetic and paramagnetic components of the nuclear magnetic shielding constant tensor  $\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^d + \sigma_{\alpha\beta}^p$ . Thus

$$\sigma_{\alpha\beta}^d = -\frac{1}{2c^2} \sum_k \int \Psi^{(00)} \frac{\mathbf{r}_{kN} \cdot \mathbf{r}_{kG} \delta_{\alpha\beta} - \mathbf{r}_{kN}^\alpha \mathbf{r}_{kG}^\beta}{r_{kN}^3} \Psi^{(00)} d\tau, \quad (4)$$

$$\sigma_{\alpha\beta}^p = -i \sum_k \left[ \frac{1}{2} \int \Psi^{(00)} I_{kG}^\alpha \Psi_\beta^{(01)} d\tau + \frac{1}{c^2} \sum_k \int \Psi^{(00)} \frac{I_{kN}^\beta}{r_{kN}^3} \Psi_\alpha^{(10)} d\tau \right], \quad (5)$$

and for the components of the magnetizability tensor  $\chi_{\alpha\beta} = \chi_{\alpha\beta}^d + \chi_{\alpha\beta}^p$

$$\chi_{\alpha\beta}^d = -\frac{1}{4} \sum_k \int \Psi^{(00)} (\mathbf{r}_{kG}^2 \delta_{\alpha\beta} - \mathbf{r}_{kG}^\alpha \mathbf{r}_{kG}^\beta) \Psi^{(00)} d\tau, \quad (6)$$

$$\chi_{\alpha\beta}^p = -i \sum_k \left[ \int \Psi^{(00)} I_{kG}^\alpha \Psi_\beta^{(10)} d\tau + \int \Psi^{(00)} I_{kG}^\beta \Psi_\alpha^{(10)} d\tau \right]. \quad (7)$$

The first-order functions  $\Psi_\alpha^{(10)}, \Psi_\beta^{(01)}$  are obtained as variational solutions of the corresponding equations

$$(\mathcal{H}^{(00)} - E^{(00)}) \Psi_\alpha^{(10)} = \frac{i}{2} \sum_k I_{kG}^\alpha \Psi^{(00)}, \quad (8)$$

$$(\mathcal{H}^{(00)} - E^{(00)}) \Psi_\beta^{(01)} = \frac{i}{c^2} \sum_k \frac{I_{kN}^\beta}{r_{kN}^3} \Psi^{(00)}, \quad (9)$$

with the unperturbed Hamiltonian  $\mathcal{H}^{(00)}$  and its eigenvalue  $E^{(00)}$  and eigenfunction  $\Psi^{(00)}$ , by minimizing the following functionals [9]:

$$I_\alpha(\Psi_\alpha^{(10)}) = \int \Psi_\alpha^{(10)} (\mathcal{H}^{(00)} - E^{(00)}) \Psi_\alpha^{(10)} d\tau + 2 \int \Psi_\alpha^{(10)} \left[ -\frac{i}{2} \sum_k I_{kG}^\alpha \right] \Psi^{(00)} d\tau, \quad (10)$$

$$I_\beta(\Psi_\beta^{(01)}) = \int \Psi_\beta^{(01)} (\mathcal{H}^{(00)} - E^{(00)}) \Psi_\beta^{(01)} d\tau + 2 \int \Psi_\beta^{(01)} \left[ -\frac{i}{c^2} \sum_k \frac{I_{kN}^\beta}{r_{kN}^3} \right] \Psi^{(00)} d\tau. \quad (11)$$

In Eqs. (5) and (7) the definition of the electronic angular momentum operator is  $I = -i\hbar\mathbf{r} \times \nabla$  and  $I_{kG}^\alpha$  and  $I_{kN}^\beta$  are components of this operator referred to the origins  $G$  and  $N$ , respectively.

Although both  $\sigma$  and  $\chi$  are physically gauge independent, in practical calculations with finite basis sets they show a dependence on the choice of gauge origin. The problem has been approximately solved by means of the individual gauge for localized orbitals (IGLO), localized orbital, localized origin (LORG), or gauge-invariant atomic orbital (GIAO) procedures [10], and recently a formal solution in terms of polarization propagator theory has been proposed [11]. Oddershede and Geertsen have developed the idea of “the gauge constant” as a measure of the gauge origin dependence of  $\sigma$  [12]. A similar quantity can be defined also for  $\chi$ . The gauge origin transformation,  $N_x = G_x - d_x$ , applied to a hydrogen molecule placed along the  $x$  axis and inserted into (4)–(7) gives

$$\sigma^d(G) = \sigma^d(N) + d_x C_\sigma^d, \quad C_\sigma^d = -\frac{2}{3} \int \Psi^{(00)} \frac{x_{1N}}{r_{1N}^3} \Psi^{(00)} d\tau, \quad (12)$$

$$\sigma^p(G) = \sigma^p(N) + d_x C_\sigma^p, \quad C_\sigma^p = -\frac{2}{3} \int \Psi^{(00)} \frac{\partial}{\partial z} \Psi_z^{(01)} d\tau, \quad (13)$$

$$\chi^d(G) = \chi^d(N) + d_x^2 C_\chi^d, \quad C_\chi^d = -\frac{1}{3}, \quad (14)$$

$$\chi^p(G) = \chi^p(N) + d_x^2 C_\chi^p, \quad C_\chi^p = -\frac{8}{3} \int \Psi^{(00)} \frac{\partial}{\partial z} \Psi_z d\tau, \quad (15)$$

where  $\Psi_z$  is a variational solution of the equation  $(\mathcal{H}^{(00)} - E^{(00)})\Psi_z = -\partial\Psi^{(00)}/\partial z$ . Obviously, for a complete basis set, the gauge constants  $C_\sigma = C_\sigma^d + C_\sigma^p$  and  $C_\chi = C_\chi^d + C_\chi^p$  are zero. All deviations from these condi-

tions cause the unphysical gauge origin dependence of the total  $\sigma$  and  $\chi$ .

The variation-perturbation method briefly outlined above has been applied to the calculation of the shielding tensor of the proton in the  $\text{H}_2$  molecule. To assess the accuracy of the present shielding results, calculations of  $\chi$  and several other expectation values have been performed with the same type of wave function. For the hydrogen molecule in its  $X^1\Sigma_g^+$  ground state the equilibrium distance  $R_e = 1.4011$  a.u. was assumed. The gauge origin  $G$  was chosen at the molecular midpoint. The zeroth-order functions used are described in Table I. The functions labeled 118–504 do not contain correlation factors so they are of CI type. The last function referred to as 586 contains explicit correlation factors, as specified in the table. The nonlinear parameters of the unperturbed functions were optimized with respect to the ground-state energy by the method described in Ref. [8]. The final results have been obtained with the 586 function.

The first-order functions,  $\Psi_z^{(10)}$  and  $\Psi_z^{(01)}$ , possess  $\Pi_g$  symmetry while  $\Psi_z$  possesses  $\Pi_u$ . The required symmetry is ensured by taking proper Gaussian products in the geminal functions  $F_i$  [Eq. (1)]. In the present calculations the following types of geminal functions have been involved:  $sp_z$ ,  $p_x p_z$ ,  $d_x^2 p_z$ ,  $p_y d_{yz} + p_z d_{z^2}$ ,  $p_z d_{y^2} + p_z d_{z^2}$ ,  $d_x^2 d_{xz}$ ,  $p_x d_{xz}$ , and  $sd_{xz}$ . The perturbation corrections relative to the noncorrelated zeroth-order functions are also limited to the noncorrelated geminal functions. Detailed discussion and examples of how to build the geminal functions are given in the previous paper [8]. Initially, the first-order functions were constructed from the bases of the three lowest eigenstates of proper symmetry, i.e., the nonlinear parameters of the basis functions were found by the optimization with respect to the energies of these eigenstates. Such a procedure was successful in the case of the dynamic polarizability calculations [13] yielding excellent agreement with the most accurate results [5,14] for both ground and excited states. However, it failed when applied to the paramagnetic components. In that case, and especially for  $\sigma^p$ , the optimization of the nonlinear coefficients with respect to the computed parameters appears to be necessary. The optimization procedure was carried out until convergence to at least four significant figures was reached, which corresponded to about 100 expansion terms.

The behavior of the calculated quantities with the change of  $\Psi^{(00)}$  is shown in Table II. It is known that an

TABLE I.  $\Psi^{(00)}$  basis definitions.  $N_0$  stands for a number of basis functions.  $E^{(00)}$  is given in hartrees. Note that only the last function contains correlation factors  $r_{12}$ .

$N_0$	$E^{(00)}$	Definition
118	-1.172 128	70 geminal functions of the type $ss$ , 16 of $sp_x$ , 16 of $p_x p_x$ , 16 of $p_y p_y + p_z p_z$
372	-1.174 059	Geminal functions of 35 different types generated from Gaussian functions $s$ through $f^a$
504	-1.174 104	CIVB corresponding to $10s4p2d1f$ full CI
586	-1.174 470	504 augmented by 82 most important $r_{12}$ terms

<sup>a</sup>See Ref. [8] for details.

TABLE II. Convergence of the magnetic shielding (in ppm) and gauge constant components (in ppm  $a_0^{-1}$ ) with the  $\Psi^{(00)}$  basis size,  $N_0$ .  $C_\sigma^p$  and  $C_\sigma^d$  stand for the gauge constants for the perpendicular components of  $\sigma^p$  and  $\sigma^d$  [see Eqs. (12) and (13)], respectively.

$N_0$	$\sigma_1^d$	$\sigma_{\parallel}^d$	$\sigma_1^p$	$\frac{3}{2}C_\sigma^p$	$-\frac{3}{2}C_\sigma^d$ <sup>a</sup>	$-C_\sigma$
118	25.223	27.870	0.9727	13.373	13.401	0.019
372	25.154	27.884	0.9889	13.505	13.541	0.024
504	25.153	27.878	0.9897	13.507	13.547	0.027
586	25.151	27.882	1.0021	13.537	13.557	0.013

<sup>a</sup>For the exact wave function, the Hellmann-Feynman theorem gives  $\frac{3}{2}C_\sigma^d = -13.563$  ppm  $a_0^{-1}$ .

accurate zeroth-order wave function is necessary when a precise variational solution of the first-order perturbation equations is required. A regular approach of the paramagnetic parameters to the exact value can be observed when better and better  $\Psi^{(00)}$  functions are employed. The accuracy of the wave function also affects expectation values, but no regular trend in  $\sigma_{\parallel}^d$  and  $\sigma_1^d$  can be established. The goodness of the set of functions applied can also be characterized by the gauge constant  $C_\sigma$ . The closer to zero is the gauge constant, the less gauge dependent are the calculations. The perpendicular component of  $\sigma^p$  depends linearly on the gauge displacement  $d_x = G_x - H_x$ :  $\sigma_{\perp}^p(G) = \sigma_{\perp}^p(H) + \frac{3}{2}C_\sigma^p d_x$ , and analogously for diamagnetic components. Table II contains values of  $\frac{3}{2}C_\sigma^p$  and  $\frac{3}{2}C_\sigma^d$  according to the convention above. The exact value of the diamagnetic part of the gauge constant,  $C_\sigma^d$ , is known (see Table II) and an estimate of the quality of  $\Psi^{(00)}$  can be performed. The converged value of the paramagnetic gauge constant,  $C_\sigma^p$ , tends to approach the corresponding negative diamagnetic value in order to minimize the total  $C_\sigma$ . Results of these attempts are given in the last column of the table. The absolute value of the gauge constant  $C_\sigma$  increases with increasing basis

size, except for the last step. This counterintuitive phenomenon illustrates the fact that only the exact zeroth-order wave function assures validity of the variational principle for the solutions of Eqs. (8) and (9). Therefore a poor zeroth-order function can accidentally yield results of second-order parameters close to the exact values.

Table III presents selected expectation values compared with the best results obtained with the Kołos-Wolniewicz wave function. The highest relative difference does not exceed 0.05%. The values of  $\langle x/r^3 \rangle$ ,  $\langle x^2/r^3 \rangle$ , and  $\langle z^2/r^3 \rangle$  are computed with a wave function of high quality. Accuracy of the electric field (about 0.05% of relative error) is examined by a comparison with the exact value, which can be derived from the Hellmann-Feynman theorem. At equilibrium, by definition, the total electric field affecting the nucleus is zero, thus a contribution coming from one electron is  $1/2R_e^2 = 0.254702$  a.u. The two latter quantities are estimated by a summation to  $\langle 1/r \rangle$ , which when compared to the most accurate known value gives a relative deviation of only 0.0007%. Also the components of  $\chi^d$  and  $\chi^p$  agree very well with those evaluated with the Kołos-Wolniewicz wave function [15]. The imperceptibly small  $C_\chi$  guarantees independence of the presented results from the choice of gauge origin. The two total magnetizabilities, the first computed with the gauge at a nucleus and the second according to the transformation formulas (14) and (15), differ by approximately 0.02%. The brief discussion above together with the results listed in Table III entitles us to believe that the results of the shielding calculations are of the same quality as those of  $\chi$ .

In Table IV the final results concerning  $\sigma$  are listed along with other theoretical and experimental values. Most of the theoretical results were obtained without taking into account electron correlation effects. Among these, coupled Hartree-Fock results of Iwai and Saika [20] and Sadlej and Raynes [21], who used large basis sets

TABLE III. Comparison of expectation values (in a.u.) and the magnetizability components (in  $e^2 a_0^2 / 2m$ ) obtained with the  $N_0 = 586$  wave function to the best results available in the literature. All entries given for  $R_e = 1.4011a_0$ .  $\Delta_\chi = \chi_{\parallel} - \chi_{\perp}$ .  $G$  and  $H$  stand for the molecular midpoint and the proton, respectively.

	Present	[3] <sup>c</sup>		Present	[15] <sup>c</sup>
$-E^{(00)}$	1.174 470 <sup>a</sup>	1.174 475	$-\chi_{\parallel}^d$	1.523 949	1.523 951
$x_G^2$	1.024 242	1.023 758	$-\chi_{\perp}^d(G)$	1.786 216	1.786 196
$z_G^2$	0.761 975	0.762 004	$\chi_{\perp}^d(H)$	2.276 986	
$r_G^2$	2.548 191	2.547 766	$\chi_{\perp}^p(G)$	0.053 436	0.053 463
$r_H^2$	3.038 961	3.038 537	$\chi_{\perp}^p(H)$	0.543 681	
$1/r_H$	0.912 446	0.912 452	$-\chi(G)$	1.663 170	1.663 139
$x_H/r_H^3$	0.254 579 <sup>b</sup>		$-\chi(H)$	1.663 523	
$x_H^2/r_H^3$	0.388 860		$\Delta_\chi(G)$	0.208 831	0.208 782
$z_H^2/r_H^3$	0.261 793		$\Delta_\chi(H)$	0.209 361	
			$-C_\chi$ <sup>c</sup>	0.000 713	

<sup>a</sup>The latest value is 1.174 475 88 hartree, interpolated from the data given in [18].

<sup>b</sup>From the Hellmann-Feynman theorem  $\langle x_H/r_H^3 \rangle = 1/2R_e^2 = 0.254702a_0^{-2}$ .

<sup>c</sup> $C_\chi$  in units of  $e^2/2m$ .

<sup>d</sup>Explicitly correlated wave functions in elliptic coordinates.

TABLE IV. Comparison of the components of the magnetic shielding constant (in ppm) obtained with the  $N_0=586$  wave function to the best results available in the literature. Unless indicated, all entries given for  $R_e = 1.4011a_0$ .

	Present	[19] <sup>c</sup>	[20] <sup>f</sup>	[20] <sup>g</sup>	[21] <sup>b,g</sup>	[22] <sup>c</sup>	[23] <sup>g</sup>	[24] <sup>b,h</sup>	[25] <sup>c,e</sup>	Experiment
$\sigma_{\parallel}^d$	27.8817	27.82	27.89	27.82	27.826	27.964	28.169	27.83	27.84	
$\sigma_{\parallel}^d(G)$	25.1510		25.06	24.87	24.837	26.453	25.418			
$\sigma_{\parallel}^d(H)$	34.6482	34.44	34.60	34.45	34.440		34.737	34.55	34.395	
$\sigma_{\perp}^d(G)$	1.0021		0.89	0.92	0.743	0.190	0.518			
$\sigma_{\perp}^d(H)$	-8.4814	-8.67	-8.05	-8.45	-8.296			-8.55	-8.565	-8.45±0.12[26], -8.48[25]
$\sigma(G)$	26.7293		26.60	26.46	26.329	27.083	26.680			26.24±0.17[27], 26.366±0.070[4]
$\sigma(H)$	26.7384	26.45	27.00	26.61	26.705			26.61	26.50	26.58±0.36[17], 26.43±0.60[28]
$\Delta\sigma(G)$	1.7286		1.94	2.03	2.246	1.321	2.233			
$\Delta\sigma(H)$	1.7149	2.05	1.34	1.82	1.682			1.83	2.02	
$C_{\sigma}^a$	-0.0130		-0.57	-0.20	-0.537					

<sup>a</sup>In units of ppm  $a_0^{-1}$ .

<sup>b</sup> $R_e = 1.4a_0$ .

<sup>c</sup> $R_e = 1.402a_0$ .

<sup>e</sup>Self-consistent-field (SCF) zeroth-order function, variation-perturbation method.

<sup>f</sup>Many-body perturbation theory (MBPT).

<sup>g</sup>Coupled Hartree-Fock (CHF).

<sup>h</sup>Configuration-interaction (CI) zeroth-order function, variation-perturbation method.

of similar quality ( $s$ -,  $p$ -,  $d$ -type Gaussians) seem to be the closest to the noncorrelated limit. As we can conclude, correlation effects on the particular  $\sigma$  values are rather small and do not exceed 2%. The only exception is  $\sigma_{\perp}^d(G)$ , but the true coupled Hartree-Fock (CHF) limit is in this case difficult to estimate due to the large discrepancies between the available results, even obtained with similar basis sets. In any case, our value 1.0021 differs significantly from the other published results. The equilibrium shielding cannot be directly compared with the experimental one. Assuming the trends reported by other authors [4,16,17], one can expect that applying corrections for rovibrational and temperature effects will give a value of  $\sigma(300\text{ K}) \approx \sigma_e - 0.39 = 26.34$  ppm which

can reasonably be compared with the experiment. And again, the near-zero value of the gauge constant  $C_{\sigma}$  ensures the gauge invariance of the magnetic shielding constant and of its anisotropy  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ . The difference of the shieldings computed with the gauge at the nucleus and the bond midpoint is less than 0.01 ppm or about 0.03% of relative difference.

The high quality of the wave function used and the near independence of the calculated magnetic shielding constant on the gauge origin allow us to conclude that the calculations of  $\sigma$  presented in this paper lead to accurate theoretical values.

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