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# Dependence of the multipole moments, static polarizabilities, and static hyperpolarizabilities of the hydrogen molecule on the H–H separation in the ground singlet state

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In this work, we provide values for the quadrupole moment  $\Theta$ , the hexadecapole moment  $\Phi$ , the dipole polarizability  $\alpha$ , the quadrupole polarizability  $C$ , the dipole-octopole polarizability  $E$ , the second dipole hyperpolarizability  $\gamma$ , and the dipole-dipole-quadrupole hyperpolarizability  $B$  for the hydrogen molecule in the ground singlet state, evaluated by finite-field configuration interaction singles and doubles (CISD) and coupled-cluster singles and doubles (CCSD) methods for 26 different H–H separations  $r$ , ranging from 0.567 a.u. to 10.0 a.u. Results obtained with various large correlation-consistent basis sets are compared at the vibrationally averaged bond length  $r_0$  in the ground state. Results over the full range of  $r$  values are presented at the CISD/d-aug-cc-pV6Z level for all of the independent components of the property tensors. In general, our values agree well with previous *ab initio* results of high accuracy for the ranges of H–H distances that have been treated in common. To our knowledge, for  $H_2$  in the ground state, our results are the first to be reported in the literature for  $\Phi$  for  $r > 7.0$  a.u.,  $\gamma$  and  $B$  for  $r > 6.0$  a.u., and  $C$  and  $E$  for any H–H separation outside a narrow range around the potential minimum. Quantum Monte Carlo values of  $\Theta$  have been given previously for H–H distances out to 10.0 a.u., but the statistical error is relatively large for  $r > 7.0$  a.u. At the larger  $r$  values in this work,  $\alpha_{xx}$  and  $\alpha_{zz}$  show the expected functional forms, to leading order in  $r^{-1}$ . As  $r$  increases further,  $\Theta$  and  $\Phi$  vanish, while  $\alpha$ ,  $\gamma$ , and the components of  $B$  converge to twice the isolated-atom values. Components of  $C$  and  $E$  diverge as  $r$  increases. Vibrationally averaged values of the properties are reported for all of the bound states (vibrational quantum numbers  $v = 0–14$ ) with rotational quantum numbers  $J = 0–3$ . Published by AIP Publishing. <https://doi.org/10.1063/1.5066308>

## I. INTRODUCTION

We have investigated the variation of the static electric properties of the hydrogen molecule with the H–H distance  $r$  in the ground singlet state, using finite-field configuration interaction singles and doubles (CISD) methods and large correlation consistent basis sets.<sup>1–3</sup> In this work, we provide values of each of the independent tensor components of the quadrupole moment  $\Theta$ , the hexadecapole moment  $\Phi$ , the dipole polarizability  $\alpha$ , the quadrupole polarizability  $C$ , the dipole-octopole polarizability  $E$ , the second hyperpolarizability  $\gamma$ , and the dipole-dipole-quadrupole polarizability  $B$ .<sup>4–6</sup> Bishop and Lam<sup>7</sup> have noted the need for values of electronic properties over a wide range of  $r$  values, for vibrational averaging. For  $\Theta$ ,  $\Phi$ ,  $C$ ,  $E$ ,  $\gamma$ , and  $B$ , our results accordingly cover a wider range of  $r$  than in previous studies.

We use the earlier, highly accurate values for  $\Theta$ ,  $\Phi$ , and  $\alpha$  to test the methodology. We then provide the first results for the dependence of  $C$  and  $E$  on the H–H distance away from equilibrium. We give values for the independent components of  $\gamma$  and  $B$ , obtained with basis sets that are flexible in representing the field-induced distortions of the electronic charge

distribution both parallel and perpendicular to the internuclear axis. These are the first values of  $\gamma$  and  $B$  in the range 6.0 a.u.  $< r \leq 10.0$  a.u.

Accurate results over a wide range of H–H distances are especially useful in high-temperature applications, where vibrational transition matrix elements with large quantum numbers are needed.<sup>8</sup> The results permit a test of *ab initio* calculations of pair properties that are used to derive line shapes for collision-induced absorption and light scattering,<sup>9–11</sup> by determining whether the *ab initio* results converge to the known long-range forms. Pair properties have been modeled or calculated *ab initio* and used to predict collision-induced line shapes for  $H_2$  interacting with  $H_2$ ,<sup>12–22</sup> with H,<sup>23,24</sup> with He,<sup>25–35</sup> and with other inert gas atoms.<sup>36–45</sup>

We investigate the long-range limiting values of the electric moments and susceptibilities. At long range, the distance-dependence of  $\alpha_{xx}$  and  $\alpha_{zz}$  is known through order  $R^{-8}$ , based on classical induction and dispersion mechanisms;<sup>46–48</sup> the leading term in the quadrupole<sup>49–52</sup> and hexadecapole<sup>50</sup> results from van der Waals dispersion and varies as  $r^{-6}$ .

Early theoretical<sup>53–58</sup> and experimental<sup>59–66</sup> studies of the quadrupole moment of  $H_2$  have been reviewed by Stogryn and Stogryn.<sup>67</sup> Experimental values for the  $H_2$  quadrupole have been obtained from collision-induced absorption of infrared radiation,<sup>61</sup> second virial coefficients,<sup>64</sup> and fits to cross

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sections for rotational excitation of  $\text{H}_2$  by electrons.<sup>65</sup> Values of the spin-lattice relaxation time  $T_1$  for gas mixtures containing orthohydrogen have been used to estimate the  $\text{H}_2$  quadrupole<sup>66</sup> because  $T_1$  is sensitive to the anisotropy of the potential.<sup>66</sup> The quadrupole of  $\text{H}_2$  has also been obtained from the temperature-dependent term in the field-gradient induced birefringence of  $\text{H}_2$  gas,<sup>68–71</sup> together with the polarizability anisotropy at optical frequencies. Additionally, the electronic contribution to the quadrupole has been derived from experimental values of the diamagnetic anisotropy and the high-frequency contribution to the diamagnetic susceptibility.<sup>60,61</sup> Zero-phonon transitions with  $\Delta J = 2$  have provided information on  $\Theta$  for hydrogen in the solid state.<sup>72</sup> Approximate values for the hexadecapole have been derived from the intensities of rotational transitions with  $\Delta J \geq 4$  observed in collision-induced infrared absorption.<sup>73–81</sup>

Theoretical calculations, including the work of Kołos and Wolniewicz<sup>54,55,82</sup> and Karl, Poll, and Wolniewicz<sup>83</sup> with a highly accurate, 54-term explicitly correlated wave function, have provided values of  $\Theta$  near equilibrium,<sup>71,83–92</sup> incorporating nonadiabatic effects.<sup>93</sup> *Ab initio* results have also been provided away from equilibrium (in Refs. 55, 71, 84–86, 91, 92, and 94), extending accurately to  $r = 7.0$  a.u.<sup>92</sup> The hexadecapole  $\Phi$  has been calculated accurately near equilibrium<sup>83,90,92</sup> and out to  $r = 6.0$  a.u.<sup>92</sup> or  $7.0$  a.u.<sup>83</sup> Rovibrational averages of  $\Theta$  and  $\Phi$  have been reported for  $\text{H}_2$ <sup>83,90,94–96</sup> and its isotopomers,<sup>97,98</sup> in various vibrational levels. The coefficient  $M_6$  of  $R^{-6}$  in the dispersion quadrupole has been evaluated by Fowler.<sup>52</sup> Values of  $\Theta$  for  $\text{H}_2$  in electronically excited states have been obtained out to  $r = 25$  a.u.<sup>99</sup>

The trace of the static polarizability is known experimentally from the measurements of the dielectric constant of the gas.<sup>100</sup> Experimental values are more commonly available for the frequency-dependent polarizability. From measurements of the refractive index,<sup>100</sup> Victor and Dalgarno<sup>101</sup> have obtained the thermally averaged polarizabilities of  $\text{H}_2$  at multiple wavelengths in the range from 185.46 nm to 632.8 nm.

Depolarization ratios for light scattered by gas-phase samples depend on both the trace and the anisotropy of the polarizability. Bridge and Buckingham<sup>102,103</sup> have determined the frequency-dependent polarizability anisotropy  $\alpha_{zz}(\omega) - \alpha_{xx}(\omega)$  from the Rayleigh depolarization ratio, and James and co-workers<sup>104</sup> have used the depolarization ratios of the  $Q_1(J)$  branches of the spectra (with  $J = 1, 2,$  and  $3$ ) to derive  $\alpha_{zz}(\omega) - \alpha_{xx}(\omega)$  as well. The first derivative<sup>105,106</sup> and second derivative<sup>106</sup> of the polarizability anisotropy with respect to the bond length (at equilibrium) have been obtained from vibrational Raman band intensity measurements.

Nelissen, Reuss, and Dymanus have determined the ratio between the polarizability anisotropy and the trace of the polarizability,<sup>107</sup> by investigating the force-balance conditions for beams of orthohydrogen passing through inhomogeneous electric and magnetic fields. Additional information on this method is provided in the [supplementary material](#). Nelissen *et al.* have also reviewed earlier experimental determinations of the polarizability and its anisotropy.<sup>107</sup> MacAdam and Ramsey derived the polarizability anisotropy from measurements of the quadratic Stark shifts in molecular-beam magnetic resonance

transitions.<sup>108</sup> Shelton<sup>109</sup> determined the ratios of the Raman intensities and transition polarizabilities experimentally for the first and second Raman overtones, relative to the fundamental transition. The ratios are sensitive to the polarizability anisotropy. The polarizability ratio subsequently calculated by Bishop and Pipin<sup>110</sup> for the first overtone at  $\lambda = 4581$  Å is within Shelton's experimental bounds.

Numerous *ab initio* results are available for the static polarizability  $\alpha$  from Refs. 86, 88, 89, 95, and 111–146, including full CI-level results at the equilibrium internuclear separation<sup>89</sup> and out to  $r = 6.0$  a.u.<sup>86</sup> Polarizability values are also available from calculations with a generalized James-Coolidge function<sup>120</sup> or explicitly correlated Gaussian geminals,<sup>90</sup> quantum Monte Carlo calculations,<sup>136</sup> and explicitly time-dependent CI calculations of the frequency-dependent polarizabilities.<sup>144</sup> Polarizabilities at imaginary frequencies have been evaluated<sup>135,136</sup> in order to compute dispersion energy coefficients. Recently, Raj, Hamaguchi, and Witek have undertaken a detailed computational study of both the static polarizability and the frequency-dependent polarizability of  $\text{H}_2$  as a function of the H–H distance, using an aug-*mcc*-pV6Z basis to which they added five sets of bond functions.<sup>146</sup> Nonadiabatic corrections to  $\alpha$  have been determined;<sup>121,147</sup> the work of Raj *et al.*<sup>146</sup> includes adiabatic, relativistic, and radiative corrections obtained by Wolniewicz.<sup>147</sup> The polarizabilities of low-lying excited states have also been evaluated.<sup>148–150</sup>

Experimental values of the  $\gamma$  hyperpolarizability are frequency-dependent because they have been derived from studies of degenerate four-wave mixing,<sup>151–153</sup> self-focusing,<sup>151</sup> electric-field induced second harmonic generation,<sup>154–159</sup> and third harmonic generation.<sup>160–162</sup> Measurements of the DC Kerr constant, which characterizes birefringence in an applied electric field, yield the polarizability anisotropy and the frequency-dependent  $\gamma$  hyperpolarizability.<sup>163–169</sup> The optical Kerr effect<sup>170</sup> and intensity-dependent refractive index<sup>151</sup> also depend on  $\gamma$  as a function of frequency. Calculations of the  $\gamma$  hyperpolarizability in Refs. 7, 86, 88, 89, 118, 123, 125–129, 133, 134, 138, 163, 171, and 172 include full CI studies for H–H distances as large as  $r = 6.0$  a.u.<sup>86</sup> Work with James-Coolidge functions extends out to  $r = 2.4$  a.u. in one case<sup>125</sup> and  $r = 4.0$  a.u. in the second case.<sup>126</sup>

The higher-order susceptibilities B, C, and E have not been studied as extensively as  $\alpha$  and  $\gamma$ . The tensor  $B(-\omega; \omega, 0)$  determines the temperature-independent contribution to field-gradient induced birefringence,<sup>68–71,173</sup> which has been measured for hydrogen molecules in the gas phase.<sup>70,163</sup> In combination with the imaginary-frequency polarizability, the B tensor at imaginary frequencies yields the van der Waals dispersion contribution to the dipole moment for  $\text{H}_2$ – $\text{H}_2$  pairs in noncentrosymmetric configurations and for  $\text{H}_2$ –H,  $\text{H}_2$ –He, and  $\text{H}_2$ –inert gas pairs.<sup>51,80,81,174–182</sup> Good approximations to dispersion dipoles have been obtained from the static polarizability, static B tensor, and dispersion energy coefficients.<sup>80,81</sup> The B and E tensors contribute to the spherical tensor coefficients for collision-induced absorption and collision-induced light scattering by  $\text{H}_2$  molecules interacting at long range (see Sec. IV). Quadrupole-induced-quadrupole interactions

depend on the C tensor; they affect intermediate-range energies of H<sub>2</sub>-H<sub>2</sub> pairs and contribute to the total energy of solid H<sub>2</sub>.<sup>72</sup>

Berns and Wormer<sup>86</sup> have calculated the independent components of B out to r = 6.0 a.u. The tensors B, C, and E are all known at equilibrium; see Refs. 7, 85, 87–89, 117, 128, 129, 135, 136, and 171 for C, Refs. 85, 88, 117, and 135 for E, and Refs. 7, 86, 88, 128, 129, 171, and 179 for B. Self-consistent field values of B, C, and E are available for r values quite close to equilibrium.<sup>88</sup> Although it has been reported that C has been calculated with a James-Coolidge wave function for values of r from 0.4 a.u. to 3.0 a.u., only the values for r = 1.4 a.u. have been tabulated earlier.<sup>128</sup>

The current work also includes the results for the matrix elements of the moments and susceptibilities in rovibrational states with quantum numbers v = 0–14 and J = 0–3, for the first time covering the full range of v values.<sup>183</sup> Raj *et al.* have recently determined the matrix elements for a wider range of J values, J = 0–15, but a narrower range of vibrational quantum numbers, v = 0–4, based on their *ab initio* results.<sup>146</sup>

Collision-induced dipoles Δμ of H<sub>2</sub>-H, H<sub>2</sub>-He, and H<sub>2</sub>-H<sub>2</sub> are needed in astrophysical studies of the radiative profiles of cool white dwarf stars at temperatures up to 7500 K.<sup>8,184–188</sup> At these temperatures, induced-dipole transition matrix elements to high-lying vibrational states (with v up to 8) come into play. Our results for the r<sub>H-H</sub> dependence of the H<sub>2</sub> property tensors, with H<sub>2</sub> substantially stretched or compressed from its equilibrium bond length, will be used to test the accuracy of *ab initio* results for Δμ at larger H<sub>2</sub>-X distances (see, e.g., Ref. 25).

## II. METHODOLOGY

The Hamiltonian for a molecule in a static field **F**, field gradient **F'**, and higher gradients **F''** and **F'''** is given in terms of the dipole, quadrupole, octopole, and hexadecapole moment operators  $\hat{\mu}$ ,  $\hat{\Theta}$ ,  $\hat{\Omega}$ , and  $\hat{\Phi}$ , respectively, by<sup>4–6</sup>

$$\hat{H} = \hat{H}_0 - \hat{\mu}_\alpha F_\alpha - (1/3)\hat{\Theta}_{\alpha\beta}F'_{\alpha\beta} - (1/15)\hat{\Omega}_{\alpha\beta\gamma}F''_{\alpha\beta\gamma} - (1/105)\hat{\Phi}_{\alpha\beta\gamma\delta}F'''_{\alpha\beta\gamma\delta} - \dots, \quad (1)$$

where H<sub>0</sub> is the Hamiltonian of the unperturbed molecule. The Greek subscripts run over the Cartesian coordinates; the Einstein convention of summation over repeated Greek subscripts is followed here and below. The operators are<sup>4–6</sup>

$$\hat{\mu}_\alpha = \sum_i q_i r_{i\alpha}, \quad (2)$$

$$\hat{\Theta}_{\alpha\beta} = (1/2) \sum_i q_i (3r_{i\alpha}r_{i\beta} - \delta_{\alpha\beta}r_i^2), \quad (3)$$

$$\hat{\Omega}_{\alpha\beta\gamma} = (1/2) \sum_i q_i [5r_{i\alpha}r_{i\beta}r_{i\gamma} - (\delta_{\alpha\beta}r_{i\gamma} + \delta_{\alpha\gamma}r_{i\beta} + \delta_{\beta\gamma}r_{i\alpha})r_i^2], \quad (4)$$

$$\begin{aligned} \hat{\Phi}_{\alpha\beta\gamma\delta} = (1/8) \sum_i q_i [ & 35r_{i\alpha}r_{i\beta}r_{i\gamma}r_{i\delta} - 5(\delta_{\alpha\beta}r_{i\gamma}r_{i\delta} + \delta_{\alpha\gamma}r_{i\beta}r_{i\delta} \\ & + \delta_{\alpha\delta}r_{i\beta}r_{i\gamma} + \delta_{\beta\gamma}r_{i\alpha}r_{i\delta} + \delta_{\beta\delta}r_{i\alpha}r_{i\gamma} + \delta_{\gamma\delta}r_{i\alpha}r_{i\beta})r_i^2 \\ & + (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})r_i^4], \end{aligned} \quad (5)$$

where the sum runs over all of the electrons and nuclei (4 total in this case) with charges q<sub>i</sub> and positions **r**<sub>i</sub>. With the

Hamiltonian in Eq. (1) and with the center of nuclear charge taken as the origin, the energy of the hydrogen molecule is given by<sup>4–6</sup>

$$\begin{aligned} E = E_0 - (1/3)\Theta_{\alpha\beta}F'_{\alpha\beta} - (1/105)\Phi_{\alpha\beta\gamma\delta}F'''_{\alpha\beta\gamma\delta} \\ - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - (1/6)C_{\alpha,\beta,\gamma\delta}F'_{\alpha\beta}F'_{\gamma\delta} \\ - (1/15)E_{\alpha,\beta,\gamma\delta}F_\alpha F''_{\beta\gamma\delta} - (1/6)B_{\alpha,\beta,\gamma\delta}F_\alpha F_\beta F'_{\gamma\delta} \\ - (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta - \dots \end{aligned} \quad (6)$$

in terms of the permanent quadrupole moment Θ, the permanent hexadecapole moment Φ, the dipole polarizability α, the quadrupole polarizability C, the dipole-octopole polarizability E, the dipole-dipole-quadrupole hyperpolarizability B, and the second dipole hyperpolarizability γ.<sup>4–6</sup> For species that lack a center of symmetry, other terms appear in the series expansion to the same orders as in Eq. (6), including the permanent dipole moment μ, the permanent octopole moment Ω, the dipole-quadrupole polarizability A, the first dipole hyperpolarizability β, and a dipole-quadrupole-quadrupole polarizability Q.<sup>4–6</sup> Only the first nonvanishing moment of a molecule is origin independent;<sup>4–6</sup> so, for example, terms containing Ω and A will also appear in the energy of an HD, HT, or DT molecule, if the center of mass rather than the center of nuclear charge is taken as the origin. In addition, these molecules have small dipole moments and higher-order odd moments due to the breakdown of the Born-Oppenheimer approximation.<sup>189</sup>

From Eq. (6), the moments and susceptibilities of the hydrogen molecule can be obtained as the formal derivatives

$$\Theta_{\alpha\beta} = -3(\partial E/\partial F'_{\alpha\beta}), \quad (7)$$

$$\Phi_{\alpha\beta\gamma\delta} = -105(\partial E/\partial F'''_{\alpha\beta\gamma\delta}), \quad (8)$$

$$\alpha_{\alpha\beta} = -(\partial^2 E/\partial F_\alpha \partial F_\beta), \quad (9)$$

$$C_{\alpha,\beta,\gamma\delta} = -3(\partial^2 E/\partial F'_{\alpha\beta} \partial F'_{\gamma\delta}), \quad (10)$$

$$E_{\alpha,\beta,\gamma\delta} = -15(\partial^2 E/\partial F_\alpha \partial F''_{\beta\gamma\delta}), \quad (11)$$

$$B_{\alpha,\beta,\gamma\delta} = -3(\partial^3 E/\partial F_\alpha \partial F_\beta \partial F'_{\gamma\delta}), \quad (12)$$

and

$$\gamma_{\alpha\beta\gamma\delta} = -(\partial^4 E/\partial F_\alpha \partial F_\beta \partial F_\gamma \partial F_\delta), \quad (13)$$

with the derivatives evaluated at zero field and zero field gradients. If the molecule is oriented along the z axis, then the permanent quadrupole has a single independent component Θ<sub>zz</sub> with Θ<sub>xx</sub> = Θ<sub>yy</sub> = -(1/2)Θ<sub>zz</sub>; the remaining components of this tensor vanish.<sup>4–6</sup> Similarly, the permanent hexadecapole has a single independent component Φ<sub>zzzz</sub>; the relationships of the other nonvanishing components to Φ<sub>zzzz</sub> have been given by Buckingham<sup>4</sup> and by McLean and Yoshimine.<sup>5</sup> The polarizability has independent components α<sub>zz</sub> and α<sub>xx</sub>; C has independent components C<sub>zz,zz</sub>, C<sub>xx,xx</sub>, and C<sub>xz,xz</sub>;<sup>4,5</sup> E has independent components E<sub>z,zzz</sub> and E<sub>x,xxx</sub>;<sup>4,5</sup> B has independent components B<sub>z,z,zz</sub>, B<sub>x,x,zz</sub>, B<sub>x,z,xz</sub>, and B<sub>x,x,xx</sub>; and γ has independent components γ<sub>zzzz</sub>, γ<sub>xxzz</sub>, and γ<sub>xxxx</sub>.<sup>4,5</sup> The relationships of the other non-zero components of these tensors to the listed components are determined by the molecular symmetries and by the properties of the quadrupole and octopole operators under contraction of two indices. For α, C, E, and

$\gamma$ , the relationships are given in Refs. 4 and 5; for  $\mathbf{B}$ , the corresponding relationships have been derived by Bohr and Hunt.<sup>80</sup>

Equations (9) and (13) are directly useful as is; Eqs. (7), (8), and (10)–(12) are formal equations that do not incorporate the requirements that the trace of the field gradient tensor must vanish and that the result of contracting any two indices in the higher-order gradient tensors must be zero.<sup>4</sup> For example, since  $\Theta_{xx} = \Theta_{yy} = -(1/2) \Theta_{zz}$ ,  $\Theta_{\alpha\beta} = 0$  for  $\alpha \neq \beta$ , and  $F'_{\alpha\alpha} = 0$ , the net energy shift due to an applied field

gradient is given by  $\Delta E = -(1/2) \Theta_{zz} F'_{zz}$ , and thus,  $dE/dF'_{zz} = -(1/2) \Theta_{zz}$  [rather than  $dE/dF'_{zz} = -(1/3) \Theta_{zz}$ ]. To take the symmetries of  $F'$  and higher gradients into account, we have imposed uniform fields and added perturbing potentials [ $z^2 - (1/2)(x^2 + y^2)$ ], [ $x^2 - (1/2)(y^2 + z^2)$ ],  $xz$ , [ $z^3 - (3/2)z(x^2 + y^2)$ ], [ $x^3 - (3/2)x(y^2 + z^2)$ ], and [ $z^4 + (3/8)(x^4 + y^4) + (3/4)x^2y^2 - 3z^2(x^2 + y^2)$ ], multiplied by parameters  $f$ ,  $g$ , and  $h$ . Then we have evaluated the derivatives of the energy  $E$  with respect to these parameters, using the finite-difference approximations,

$$\partial E/\partial f = 1/(f_1)[E(f_1) - E(-f_1)] - 1/(2f_2)[E(f_2) - E(-f_2)], \quad (14)$$

$$\partial^2 E/\partial f^2 = 2/(f_1^2)[E(f_1) + E(-f_1) - 2E(0)] - 1/(f_2^2)[E(f_2) + E(-f_2) - 2E(0)], \quad (15)$$

$$\begin{aligned} \partial^2 E/\partial f \partial g &= 1/(2f_1 g_1)[E(f_1, g_1) + E(-f_1, -g_1) - E(f_1, -g_1) - E(-f_1, g_1)] \\ &\quad - 1/(4f_2 g_2)[E(f_2, g_2) + E(-f_2, -g_2) - E(f_2, -g_2) - E(-f_2, g_2)], \end{aligned} \quad (16)$$

$$\begin{aligned} \partial^3 E/\partial f^2 \partial g &= 1/(f_1^2 g_1)[E(f_1, g_1) + E(-f_1, g_1) - E(-f_1, -g_1) - E(f_1, -g_1) + 2E(0, -g_1) - 2E(0, g_1)] \\ &\quad - 1/(2f_2^2 g_2)[E(f_2, g_2) + E(-f_2, g_2) - E(-f_2, -g_2) - E(f_2, -g_2) + 2E(0, -g_2) - 2E(0, g_2)], \end{aligned} \quad (17)$$

$$\begin{aligned} \partial^3 E/\partial f \partial g \partial h &= 1/(4f_1 g_1 h_1)[E(f_1, g_1, h_1) + E(-f_1, -g_1, h_1) + E(-f_1, g_1, -h_1) + E(f_1, -g_1, -h_1) \\ &\quad - E(-f_1, -g_1, -h_1) - E(-f_1, g_1, h_1) - E(f_1, -g_1, h_1) - E(f_1, g_1, -h_1)] \\ &\quad - 1/(8f_2 g_2 h_2)[E(f_2, g_2, h_2) + E(-f_2, -g_2, h_2) + E(-f_2, g_2, -h_2) + E(f_2, -g_2, -h_2) \\ &\quad - E(-f_2, -g_2, -h_2) - E(-f_2, g_2, h_2) - E(f_2, -g_2, h_2) - E(f_2, g_2, -h_2)], \end{aligned} \quad (18)$$

$$\begin{aligned} \partial^4 E/\partial f^4 &= 2/(f_1^4)[E(2f_1) + E(-2f_1) - 4E(f_1) - 4E(-f_1) + 6E(0)] \\ &\quad - 1/(f_2^4)[E(2f_2) + E(-2f_2) - 4E(f_2) - 4E(-f_2) + 6E(0)], \end{aligned} \quad (19)$$

where  $f_2 = 2^{1/2} f_1$ ,  $g_2 = 2^{1/2} g_1$ , and  $h_2 = 2^{1/2} h_1$ . To compute  $\gamma_{xxxz}$  ( $f = F_x$ ,  $g = F_z$ ), we have used

$$\begin{aligned} \partial^4 E/\partial f^2 \partial g^2 &= 8/(f_1^2 g_1^2)[E(f_1, g_1) - E(f_1, 0) - E(0, g_1) + E(0, 0)] \\ &\quad - 4/(f_1^2 g_1^2)[E(f_2, g_2) - E(f_2, 0) - E(0, g_2) + E(0, 0)]. \end{aligned} \quad (20)$$

The result in Eq. (20) has been simplified by the use of symmetry; the energy is identical in the field  $\mathbf{F}$  and the field  $-\mathbf{F}$ . The errors in these equations are of order  $f^m g^n h^p$ , with  $m + n + p = 4$ . The errors are essentially negligible if  $f$ ,  $g$ , and  $h$  are sufficiently small. At the same time, these parameters must be sufficiently large to give results that are numerically significant, yet not so large that convergence issues arise. After numerical experimentation, we have chosen a dipole field intensity of  $10^{-3}$  a.u. for  $\alpha$  and  $\mathbf{E}$ , quadrupolar perturbations of  $10^{-4}$  a.u. for  $\Theta$  and  $\mathbf{C}$ , octopolar perturbations of  $10^{-5}$  a.u. for  $\mathbf{E}$ , and hexadecapolar perturbations of  $10^{-6}$  a.u. for  $\Phi$ . To compute the hyperpolarizabilities  $\mathbf{B}$  and  $\gamma$ , we have used larger dipole and quadrupole field intensities,  $3 \cdot 10^{-3}$  a.u. and  $3 \cdot 10^{-4}$  a.u., respectively. All of these values correspond to  $f_1$ ,

$g_1$ , or  $h_1$ . The total number of individual energy calculations was limited to 22 for each H–H separation, due to the high symmetry.

For the equilibrium bond length  $r_e$  and the averaged bond length  $r_0$  in the ground vibrational state, we have calculated the energy of the perturbed system using the configuration interaction singles and doubles (CISD, which is full configuration interaction for  $H_2$ ) method. The reference wave function was obtained at the restricted Hartree-Fock (RHF) level. To assess the effect of the basis set quality on the different electric properties, we have used various correlation-consistent basis sets: cc-pV5Z ( $\equiv 5Z$ ), aug-cc-pV5Z ( $\equiv A5Z$ ), aug-cc-pV6Z ( $\equiv A6Z$ ), d-aug-cc-pVQZ ( $\equiv D4Z$ ), d-aug-cc-pV5Z ( $\equiv D5Z$ ), d-aug-cc-pV6Z ( $\equiv D6Z$ ), and t-aug-cc-pV6Z ( $\equiv T6Z$ ).<sup>1–3</sup> At  $r_0$ ,



each of the tensor components was evaluated with all seven basis sets. The D6Z and T6Z values for the properties are converged to within 1% (see Sec. III). We have used the D6Z basis set for the construction of the full energy and property curves because we encountered linear dependence in the T6Z basis at the shorter H–H distances. As an additional check on the D6Z results, we have computed all of the properties for 17 values of the H–H distance between 1.787 a.u. and 7.000 a.u. at the CISD level, using the d-aug-cc-pV6Z basis augmented by the inclusion of 6s 6p 6d 3f 1g 1h mid-bond functions.<sup>190,191</sup> The results are listed in Tables S1 and S2 of the [supplementary material](#). Typically, the D6Z results with and without mid-bond functions differ by less than 0.5%, although in a few isolated cases, differences of  $\sim 1\%$  are found. The Molpro 2015.1 suite of codes was used throughout this study.<sup>192</sup> No symmetry constraints were imposed on the wave function. The integral accuracy and the energy convergence thresholds were set to  $10^{-12}$  a.u.

James-Coolidge functions with explicit correlation have been used in earlier calculations of electrical properties (see Refs. 120, 125, 126, 128, 129, and 171). The choice of basis is important (see, e.g., Ref. 138). The behavior of the correlation consistent basis sets<sup>1–3</sup> has been examined earlier in calculations of the polarizability  $\alpha$ <sup>71,140</sup> and the quadrupole moment  $\Theta$ ,<sup>71,91</sup> but not for the other properties. Both  $\alpha$  and  $\gamma$  have been calculated previously with sum-over-states expressions, primarily due to the interest in frequency-dependent susceptibilities, which are given by sum-over-states expressions with frequency-dependent denominators (see, e.g., Refs. 114, 117, 118, 122, and 125).

### III. NUMERICAL RESULTS FOR THE H ATOM AND FOR H<sub>2</sub> NEAR THE EQUILIBRIUM BOND LENGTH

We have examined the influence of the basis set on the accuracy of the electrical properties of the hydrogen atom and of the hydrogen molecule near the equilibrium bond length. Exact, analytical results for the energy and the non-zero, symmetry-unique components of the electrical properties  $\alpha$ ,  $C$ ,  $B$ , and  $\gamma$  of the H atom are listed in Table I, along with the values obtained with seven basis sets. The 5Z basis is the smallest; its energy is too high by 5.46  $\mu\text{H}$ , and this

basis fails to reproduce any of the properties well. Adding diffuse functions to form the A5Z basis reduces the error in the energy only slightly (to 5.22  $\mu\text{H}$ ). While the A5Z basis gives  $\alpha = 4.4929$  a.u., close to the exact value  $\alpha = 9/2$  a.u., the remaining properties still do not agree well with the exact values. Increasing the cardinal number of the basis set to A6Z improves the values of the other susceptibilities, but Table I shows that a second series of diffuse functions is needed in order to obtain accurate results. The susceptibilities from the D4Z basis are already in very good agreement with the exact results, even though the energy values are not as good. The D6Z value of the energy is identical to the T6Z value (with a third series of diffuse functions added), to the number of digits shown; the remaining error in the energy is 0.72  $\mu\text{H}$ . The D6Z properties come within 0.1% of the T6Z results. Overall, the D6Z values are accurate to within 1%;  $\gamma$  is the most difficult quantity to calculate accurately in standard basis sets for the H atom.

Values are listed in Table S3 for the energy of the H<sub>2</sub> molecule at  $r_0 = 1.449$  a.u., the vibrationally averaged H–H distance in the ground rotational and vibrational state, and at  $r_e = 1.400$  a.u., the equilibrium bond length. The difference in the energies obtained with the D6Z and T6Z basis sets at  $r_0$  is only 0.12  $\mu\text{H}$ . At  $r_e$ , the results from the D6Z basis are 161  $\mu\text{H}$  below the extrapolation to the complete basis set limit from one set of CISD calculations,<sup>91</sup> but 114  $\mu\text{H}$  above the energy from valence bond calculations with explicitly correlated Gaussians.<sup>90</sup>

Values of the moments, static polarizabilities  $\alpha$ ,  $E$ , and  $C$ , and static hyperpolarizabilities  $B$  and  $\gamma$  obtained with the various basis sets are listed in Table II at  $r_0$ , along with D6Z results at  $r_e$ . In Table II, we also compare our values with accurate calculated values from the literature and with experimental results for the vibrationally averaged properties, where available.

The multipole moments  $\Theta$  and  $\Phi$  are rather insensitive to variation in the basis set (from 5Z to T6Z). The calculated quadrupole  $\Theta$  at  $r_0$  is 0.480 a.u. to within  $\sim 1\%$  in all of the basis sets used in this work, and the hexadecapole  $\Phi$  at  $r_0$  is 0.315 a.u. to within  $\sim 4\%$ . Both moments are slightly smaller at  $r_e$ . Our CISD/D6Z value of  $\Theta$  differs by only 0.006% from the value found by Buckingham, Coriani, and Rizzo<sup>71</sup> and our value of  $\Phi$  differs by 0.11% from the value given by Komasa and Thakkar.<sup>90</sup>

TABLE I. Energies, polarizabilities, and hyperpolarizabilities of the H atom at the RHF level of theory obtained with a variety of basis sets. Values are in a.u.

Quantity	5Z	A5Z	A6Z	D4Z	D5Z	D6Z	T6Z	Accurate <sup>a</sup>
$-E_0$	0.499 994 54	0.499 994 78	0.499 999 28	0.499 948 42	0.499 994 80	0.499 999 28	0.499 999 28	0.500 000 00
$\alpha^b$	3.222 6	4.492 9	4.492 8	4.500 3	4.493 2	4.492 8	4.493 1	4.500 0
$C^c$	0.821 4	3.977 1	4.487 0	4.934 6	4.970 3	4.981 3	4.985 8	5.000 0
$B^d$	-18.86	-90.38	-98.25	-106.29	-106.82	-106.86	-106.87	-106.50
$\gamma^e$	39	1 056	1 190	1 315	1 336	1 342	1 341	1 333

<sup>a</sup>Reference 194. The exact values for the listed properties are  $E_0 = -1/2$ ,  $\alpha = 9/2$ ,  $C = 5$ ,  $B = -213/2$ , and  $\gamma = 10\ 665/8$ .

<sup>b</sup> $\alpha = \alpha_{xx} = \alpha_{zz}$ .

<sup>c</sup> $C = C_{xx,xx} = C_{zz,zz} = 4/3 C_{xz,xz}$ .

<sup>d</sup> $B = B_{xx,xx} = B_{zz,zz} = -2 B_{xx,zz} = 4/3 B_{xz,xz}$ .

<sup>e</sup> $\gamma = \gamma_{xxxx} = \gamma_{zzzz} = 3 \gamma_{xxzz}$ .

TABLE II. CISD multipole moments, polarizabilities, and hyperpolarizabilities of H<sub>2</sub> at the vibrationally averaged bond length  $r_0$  and the equilibrium bond length  $r_e$  for H<sub>2</sub>, obtained with a variety of basis sets. Lit. ( $r_0$ ) lists values at the vibrationally averaged bond length in the ground rovibrational state, and Lit. ( $r_e$ ) lists values at equilibrium. Values are in a.u.

Quantity	5Z <sup>a</sup>	A5Z <sup>a</sup>	A6Z <sup>a</sup>	D4Z <sup>a</sup>	D5Z <sup>a</sup>	D6Z <sup>a</sup>	T6Z <sup>a</sup>	Lit. ( $r_0$ )	D6Z <sup>b</sup>	Lit. ( $r_e$ )	Expt.
$\Theta$	0.4776	0.4824	0.4824	0.4825	0.4822	0.4823	0.4823		0.4563	0.45633 <sup>c</sup> 0.4552 <sup>e</sup>	0.460(21) <sup>d</sup> 0.4853 <sup>f</sup>
$\Phi$	0.3048	0.3179	0.3169	0.3168	0.3119	0.3139	0.3138		0.2769	0.2772 <sup>g</sup>	
$\alpha_{xx}$	3.9321	4.7293	4.7289	4.7346	4.7291	4.7309	4.7319	4.740 <sup>h</sup>	4.5738	4.53(7) <sup>i</sup> 4.57 <sup>k</sup> 4.774 <sup>l</sup>	4.82 <sup>j</sup>
$\alpha_{zz}$	6.7340	6.7186	6.7177	6.7240	6.7192	6.7178	6.7179	6.723 <sup>h</sup>	6.3892	6.42(8) <sup>i</sup> 6.803 <sup>l</sup>	6.94 <sup>j</sup>
$E_{x,xxx}$	-1.6848	-1.7827	-1.7529	-1.8048	-1.7817	-1.7743	-1.7728	-1.774 <sup>m</sup>	-1.5868		
$E_{z,zzz}$	4.4353	4.4440	4.4666	4.4833	4.4965	4.4801	4.4797	4.442 <sup>m</sup>	3.9605		
$C_{xx,xx}$	2.1548	4.8344	5.0596	5.1629	5.1855	5.1990	5.2004	5.20 <sup>m</sup>	4.9285	4.93(24) <sup>i</sup>	
$C_{zz,zz}$	4.6091	6.3633	6.3851	6.3887	6.3925	6.3966	6.3984	6.39 <sup>m</sup>	5.9908	6.10(35) <sup>i</sup>	
$C_{xz,xz}$	3.2366	4.4484	4.4470	4.4634	4.4467	4.4474	4.4473	4.44 <sup>m</sup>	4.1847	4.30(36) <sup>i</sup>	
$B_{x,xx}$	-21.16	-66.81	-69.79	-71.21	-71.51	-71.48	-71.49		-67.02	-66.83 <sup>n</sup>	
$B_{z,zz}$	-76.67	-97.63	-97.88	-98.55	-98.21	-98.07	-98.07		-90.70	-90.29 <sup>n</sup>	
$B_{x,xz}$	14.16	36.64	37.19	36.42	36.82	36.82	36.79		34.46	34.37 <sup>n</sup>	
$B_{x,xz}$	-35.19	-63.93	-63.71	-63.95	-63.67	-63.57	-63.55		-59.17	-59.00 <sup>n</sup>	
$\gamma_{xxxx}$	50	565	606	621	641	629	630	610 <sup>o</sup>	584	579.5 <sup>n</sup> 564 <sup>o</sup>	
$\gamma_{zzzz}$	473	744	747	752	748	749	746	745 <sup>o</sup>	688	682.5 <sup>n</sup> 683 <sup>o</sup>	
$\gamma_{xxzz}$	69	236	235	233	238	232	234	219 <sup>o</sup>	214	211.9 <sup>n</sup> 200 <sup>o</sup>	

<sup>a</sup>This work,  $r = r_0$ .

<sup>b</sup>This work,  $r = r_e$ .

<sup>c</sup>Reference 71: CCSD/t-aug-cc-pVQZ.

<sup>d</sup>Reference 84: Derived from previous experimental data.

<sup>e</sup>Reference 91: CISD/CBS.

<sup>f</sup>Reference 197: Magnetic anisotropy experiments ( $v = 0/J = 1$ ).

<sup>g</sup>Reference 90: Valence bond calculations with explicitly correlated Gaussian functions.

<sup>h</sup>Reference 126: Sum-over-states method using James-Coolidge type functions.

<sup>i</sup>Reference 136: Quantum Monte Carlo.

<sup>j</sup>Reference 103: Light scattering (6328 Å wavelength).

<sup>k</sup>Reference 140: CCSD/A5Z.

<sup>l</sup>Reference 101: Sum-over-states method.

<sup>m</sup>Reference 135: Sum-over-states method using James-Coolidge type functions.

<sup>n</sup>Reference 129: Sum-over-states method using James-Coolidge type functions.

<sup>o</sup>Reference 125: Sum-over-states method using James-Coolidge type functions.

For the dipole polarizability, the CISD values obtained with the D6Z basis agree within 0.20% with the highly accurate theoretical values obtained by Bishop and Lam,  $\alpha_{xx} = 4.740$  a.u. and  $\alpha_{zz} = 6.723$  a.u.<sup>126</sup> The isotropically averaged, static polarizability in the D6Z basis ( $\bar{\alpha} = 5.393$  a.u.) is 0.81% smaller than the experimental value from the work of Victor and Dalgarno.<sup>101</sup>

The E tensor components can be estimated fairly well, even with the 5Z basis. The full range of variation of the CISD results for the six basis sets (from 5Z to T6Z) is  $\sim 6.5\%$  for  $E_{x,xxx}$  and  $\sim 1.3\%$  for  $E_{z,zzz}$ . Our CISD values with the D6Z basis set come within 1% of the accurate sum-over-states results of Bishop and Pipin,<sup>135</sup>  $E_{x,xxx} = -1.774$  a.u. and  $E_{z,zzz} = 4.442$  a.u.

By contrast, the 5Z basis is inadequate to obtain the C tensor components. Values obtained with larger basis sets vary from the CISD/5Z results by 25% or more, while results from the augmented and doubly augmented basis sets differ comparatively little from each other, as shown in Table II. Our CISD/D6Z results for  $C_{xx,xx}$  are in excellent agreement with

the literature values at  $r_e$  and  $r_0$ : We find  $C_{xx,xx} = 4.93$  a.u. at  $r_e$  compared with  $4.93 \pm 0.24$  a.u. (from Ref. 136) and  $C_{xx,xx} = 5.20$  a.u., identical to 5.20 at  $r_0$  (from Ref. 135). The CISD/D6Z values of  $C_{zz,zz}$  and  $C_{xz,xz}$  at  $r_e$  are within the estimated uncertainties of the values given in Ref. 136. At  $r_0$ , they differ by only 0.01 a.u. from the values in Ref. 135.

For the hyperpolarizabilities  $B$  and  $\gamma$ , Table II shows that the 5Z basis is again inadequate in all cases. The components of  $B$  increase dramatically in absolute value when the first series of diffuse Gaussians is added. The differences between the values of  $B_{z,zz}$ ,  $B_{x,xz}$ , and  $B_{x,xz}$  obtained with the A5Z basis and the T6Z basis are all less than 0.6%; by contrast, this difference is  $\sim 6.5\%$  for  $B_{x,xx}$ . Our CISD/D6Z results for all of the  $B$  tensor components at  $r_e$  differ by less than 0.5% from the sum-over-states values of Bishop, Pipin, and Cybulski.<sup>129</sup>

The CISD/D6Z values for the  $\gamma$  hyperpolarizability are in reasonably good agreement with the values obtained by Bishop and Pipin<sup>125</sup> with the sum-over-states method and

James-Coolidge wave functions: the results for  $\gamma_{zzzz}$  differ by  $\sim 0.5\%$ , for  $\gamma_{xxxx}$  by  $\sim 3\%$ , and for  $\gamma_{xxzz}$  by  $\sim 6\%$ , with our values higher in each case. We note however that the D6Z and T6Z values differ from each other by less than 1% and that the values obtained at  $r_e$  by Bishop, Pipin, and Cybulski,<sup>129</sup> also using the sum-over-states method with James-Coolidge wave functions, are larger than the results in Ref. 125 by 2.7% for  $\gamma_{xxxx}$  and  $\sim 6\%$  for  $\gamma_{xxzz}$ , showing the same trends as our results.

From this examination of the results for the moments and susceptibilities at  $r_0$  and  $r_e$ , we conclude that at least one series of diffuse functions in the basis set is needed in order to obtain reliable values for the electrical moments and susceptibilities. Our calculations over the full range of H–H separations have been carried out in the D6Z basis.

#### IV. DEPENDENCE OF THE MOMENTS AND SUSCEPTIBILITIES ON THE H–H DISTANCE

At the CISD/D6Z level, we have obtained the values of the properties at 26  $r_{H-H}$  distances from 0.567 a.u. to 10.0 a.u. Our results are listed in Table III for the permanent moments  $\Theta$  and  $\Phi$  and for the components of the linear response tensors  $\alpha_{xx}$ ,  $\alpha_{zz}$ ,  $E_{x,xxx}$ ,  $E_{z,zzz}$ ,  $C_{xx,xx}$ ,  $C_{zz,zz}$ , and  $C_{xz,xz}$ . Results for the hyperpolarizabilities  $B_{x,x,xx}$ ,  $B_{z,z,zz}$ ,  $B_{x,x,zz}$ ,  $B_{x,z,xz}$ ,  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xxzz}$  are listed in Table IV. The results for  $\Theta$ ,  $\Phi$ ,  $\alpha_{xx}$ , and  $\alpha_{zz}$  are plotted in Fig. 1. Results for  $E_{x,xxx}$ ,  $E_{z,zzz}$ ,  $C_{xx,xx}$ ,  $C_{zz,zz}$ ,  $C_{xz,xz}$ ,  $B_{x,x,xx}$ ,  $B_{z,z,zz}$ ,  $B_{x,x,zz}$ , and  $B_{x,z,xz}$  are plotted in Fig. 2; results for  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xxzz}$  are plotted in Fig. 3. Addition-

ally, values of the energy,  $\Theta$ ,  $\Phi$ ,  $\alpha_{xx}$ ,  $\alpha_{zz}$ ,  $E_{x,xxx}$ ,  $E_{z,zzz}$ ,  $C_{xx,xx}$ ,  $C_{zz,zz}$ , and  $C_{xz,xz}$  obtained with the d-aug-cc-pV6Z basis + 6s 6p 6d 3f 1g 1h mid-bond functions are listed for 17 values of  $r$  between 1.787 a.u. and 7.000 a.u. in Table S1 of the [supplementary material](#).<sup>190,191</sup> Results from the d-aug-cc-pV6Z basis + 6s 6p 6d 3f 1g 1h mid-bond functions for  $B_{x,x,xx}$ ,  $B_{z,z,zz}$ ,  $B_{x,x,zz}$ ,  $B_{x,z,xz}$ ,  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xxzz}$  are listed for the same range of  $r$  values in Table S2 of the [supplementary material](#).

To our knowledge, our results for the electrical properties of  $H_2$  in the ground state are the first accurate values to be reported for  $\Theta$  at H–H separations  $r > 7.0$  a.u.,  $\Phi$  for  $r > 7.0$  a.u.,  $\gamma$  and  $B$  for  $r > 6.0$  a.u., and  $C$  and  $E$  for any H–H distance outside a narrow range around the potential minimum. We have also obtained results for a larger number of H–H distances in most cases.

The values of the quadrupole  $\Theta$  agree well with the results obtained by Karl, Poll, and Wolniewicz,<sup>83</sup> Komasa and Thakkar,<sup>90</sup> the multi-reference configuration interaction (MRCI) results of Lawson and Harrison,<sup>91</sup> and the Monte Carlo results of Alexander and Coldwell<sup>92</sup> over the range of H–H distances treated in common. Figure 4 shows our values of  $\Theta$  as a function of the H–H distance, along with values from Refs. 83, 90–92. At  $r = 1.0$  a.u., literature values are  $\Theta = 0.2571$  a.u. from the work of Karl, Poll, and Wolniewicz,<sup>83</sup> 0.2566 a.u. from the work of Poll and Wolniewicz,<sup>94</sup> and 0.2563 a.u. from the work of Komasa and Thakkar,<sup>90</sup> our interpolated value is 0.2571 a.u. At  $r = 2.0$  a.u., our interpolated value of 0.7701 a.u. again compares well with the literature values 0.7705 a.u.,<sup>83</sup> 0.7704 a.u.,<sup>94</sup> and 0.7696 a.u.<sup>90</sup>

TABLE III. CISD/d-aug-cc-pV6Z energies, multipole moments, and linear response tensor elements for  $H_2$  with bond length  $r$  (all in a.u.).

$r$	$-E_0$	$\Theta$	$\Phi$	$\alpha_{xx}$	$\alpha_{zz}$	$-E_{x,xxx}$	$E_{z,zzz}$	$C_{xx,xx}$	$C_{zz,zz}$	$C_{xz,xz}$
0.567	0.701 769 64	0.0895	0.0088	2.2080	2.3922	0.1059	0.2270	1.616	1.683	1.245
0.942	1.102 935 42	0.2302	0.0628	3.1726	3.8204	0.4519	1.0334	2.788	3.082	2.231
1.111	1.152 010 22	0.3086	0.1175	3.6682	4.6607	0.7518	1.7767	3.484	3.978	2.847
1.280	1.171 223 23	0.3934	0.1993	4.1904	5.6272	1.1830	2.8873	4.289	5.076	3.583
1.449	1.173 961 17	0.4823	0.3139	4.7308	6.7178	1.7738	4.4792	5.198	6.397	4.447
1.787	1.155 986 33	0.6624	0.6582	5.8296	9.2305	3.5705	9.6547	7.323	9.824	6.595
2.125	1.126 818 50	0.8266	1.1649	6.8848	12.0240	6.4333	18.4261	9.798	14.473	9.326
2.463	1.096 964 30	0.9507	1.8052	7.8123	14.7563	10.6181	31.6949	12.515	20.520	12.641
2.801	1.070 546 24	1.0126	2.4912	8.5376	16.9525	16.3012	49.6049	15.339	28.029	16.496
3.000	1.057 267 58	1.0138	2.8629	8.8507	17.8049	20.3651	61.9475	16.990	33.078	18.987
3.200	1.045 748 22	0.9881	3.1752	9.0777	18.2552	24.9605	75.2263	18.604	38.523	21.634
3.400	1.036 031 04	0.9375	3.4012	9.2225	18.2882	30.0233	88.9156	20.149	44.213	24.406
3.600	1.028 008 64	0.8667	3.5251	9.2969	17.9453	35.4949	102.585	21.606	50.011	27.287
3.800	1.021 518 26	0.7818	3.5424	9.3162	17.3081	41.3097	115.927	22.971	55.788	30.265
4.000	1.016 364 18	0.6894	3.4604	9.2971	16.4789	47.4065	128.798	24.253	61.460	33.331
4.250	1.011 484 47	0.5729	3.2442	9.2420	15.3241	55.3512	144.251	25.766	68.356	37.278
4.500	1.007 977 98	0.4638	2.9414	9.1736	14.1821	63.6006	159.245	27.228	75.084	41.354
5.000	1.003 776 16	0.2863	2.2364	9.0483	12.2719	80.9358	189.319	30.214	88.532	49.910
5.500	1.001 768 66	0.1675	1.5788	8.9666	10.9843	99.4477	221.534	33.533	102.832	59.071
6.000	1.000 831 79	0.0948	1.0612	8.9250	10.1972	119.293	257.258	37.333	118.654	68.916
6.500	1.000 397 76	0.0527	0.6906	8.9093	9.7360	140.615	296.956	41.646	136.264	79.510
7.000	1.000 195 75	0.0291	0.4410	8.9076	9.4688	163.511	340.649	46.456	155.701	90.896
7.500	1.000 100 27	0.0161	0.2799	8.9126	9.3124	188.036	388.210	51.732	176.911	103.098
8.000	1.000 053 94	0.0090	0.1790	8.9201	9.2186	214.217	439.494	57.444	199.820	116.129
9.000	1.000 018 26	0.0031	0.0789	8.9352	9.1220	271.593	552.820	70.102	250.499	144.701
10.000	1.000 007 28	0.0012	0.0417	8.9473	9.0770	335.693	680.076	84.325	307.404	176.647



TABLE IV. CISD/d-aug-cc-pV6Z energies and hyperpolarizability tensor elements for B and  $\gamma$  of H<sub>2</sub> with bond length  $r$  (all in a.u.).

$r$	$-E_0$	$-B_{x,x,xx}$	$-B_{z,z,zz}$	$B_{x,x,zz}$	$-B_{x,z,xz}$	$\gamma_{xxxx}$	$\gamma_{zzzz}$	$\gamma_{xxzz}$
0.567	0.701 769 64	17.29	18.56	8.67	13.43	242	-77	62
0.942	1.102 935 42	33.84	40.03	17.09	27.69	264	286	94
1.111	1.152 010 22	44.37	55.10	22.54	37.29	361	402	129
1.280	1.171 223 23	56.90	74.33	29.08	49.19	481	554	173
1.449	1.173 961 17	71.49	98.05	36.82	63.57	628	750	231
1.787	1.155 986 33	106.11	159.14	55.75	99.80	1002	1 291	385
2.125	1.126 818 50	145.96	233.19	78.76	144.26	1454	2 131	590
2.463	1.096 964 30	186.83	303.88	104.28	191.82	1945	3 484	843
2.801	1.070 546 24	223.43	345.41	129.78	234.17	2403	5 664	1127
3.000	1.057 267 58	240.89	346.51	143.42	253.02	2630	7 402	1295
3.200	1.045 748 22	254.42	327.96	155.17	265.73	2811	9 407	1451
3.400	1.036 031 04	263.58	292.40	164.26	271.73	2940	11 480	1583
3.600	1.028 008 64	268.45	245.96	170.23	271.43	3017	13 359	1678
3.800	1.021 518 26	269.50	196.50	172.93	265.99	3048	14 792	1730
4.000	1.016 364 18	267.52	151.28	172.59	256.97	3042	15 615	1740
4.250	1.011 484 47	262.12	108.01	168.68	243.08	3001	15 739	1701
4.500	1.007 977 98	254.98	82.48	162.17	228.66	2939	15 025	1623
5.000	1.003 776 16	240.15	75.76	146.29	203.91	2811	12 274	1424
5.500	1.001 768 66	228.33	100.42	131.87	187.16	2715	9 332	1246
6.000	1.000 831 79	220.43	131.72	121.20	176.95	2657	7 028	1117
6.500	1.000 397 76	215.65	158.86	114.14	170.97	2627	5 442	1031
7.000	1.000 195 75	212.98	179.17	109.76	167.48	2616	4 415	978
7.500	1.000 100 27	211.63	193.16	107.21	165.41	2615	3 771	945
8.000	1.000 053 94	211.06	202.25	105.84	164.13	2618	3 375	926
9.000	1.000 018 26	211.04	211.18	104.96	162.71	2631	2 988	908
10.000	1.000 007 28	211.45	214.10	105.01	162.00	2642	2 841	901

Agreement between our values of the hexadecapole  $\Phi$  and those of Karl, Poll, and Wolniewicz<sup>83</sup> is very close over most of the range of H–H distances covered in Ref. 83; the values obtained by Karl *et al.*<sup>83</sup> are somewhat larger than ours at  $r = 3.0$  and  $4.0$  a.u. and also larger than our interpolated value at  $3.5$  a.u., but smaller than our value at  $5.0$  a.u. To compare results at shorter H–H separations, at  $r = 0.8$  a.u., our interpolated value is  $\Phi = 0.0332$  a.u., compared with  $0.0342$  a.u. from the work of Karl *et al.*<sup>83</sup> and  $0.372$  a.u. from the work of Komasa and Thakkar;<sup>90</sup> at  $r = 2.6$  a.u., our interpolated value is  $\Phi = 2.084$  a.u., compared with  $2.143$  a.u.<sup>83</sup> and  $2.090$  a.u.<sup>90</sup>

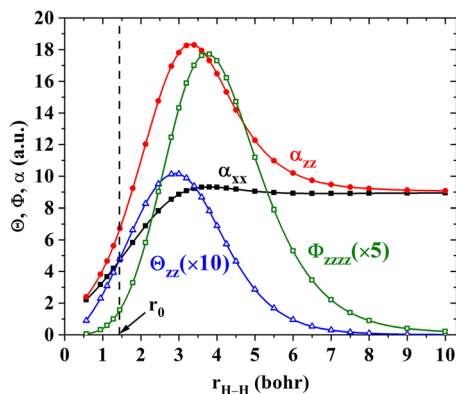


FIG. 1. CISD/D6Z results vs. the H–H distance for the quadrupole moment  $\Theta_{zz}$  (multiplied by 10), hexadecapole moment  $\Phi_{zzzz}$  (multiplied by 5), and dipole polarizabilities  $\alpha_{xx}$  and  $\alpha_{zz}$ .

Figure 5 shows our values of  $\Phi$  as a function of the H–H distance, compared with earlier *ab initio* results.<sup>83,90,92</sup>

The polarizability components  $\alpha_{xx}$  and  $\alpha_{zz}$  have been determined by Rychlewski<sup>121</sup> at 25 H–H distances between  $0.6$  a.u. and  $10.0$  a.u., with 80 terms in the unperturbed wave function and 65 in the first-order perturbed wave function, using the method of Kołos and Wolniewicz.<sup>111</sup> Our results are in very close agreement with Rychlewski's,<sup>121</sup> as shown in Fig. 6. Deviations between the Mathematica interpolations<sup>193</sup> of our results and Rychlewski's<sup>121</sup> for  $\alpha_{xx}$  range between  $0.013\%$  and  $0.156\%$ , with an average absolute difference of  $0.093\%$ . Deviations between the Mathematica

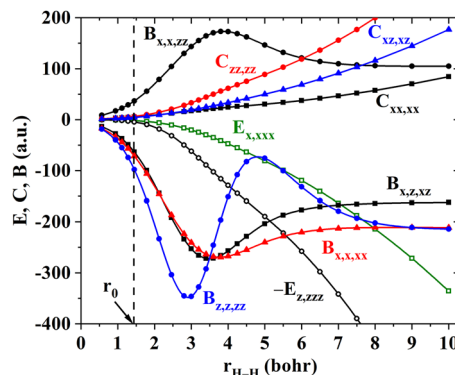


FIG. 2. CISD/D6Z results vs. the H–H distance for the different components of the E, C, and B tensors.

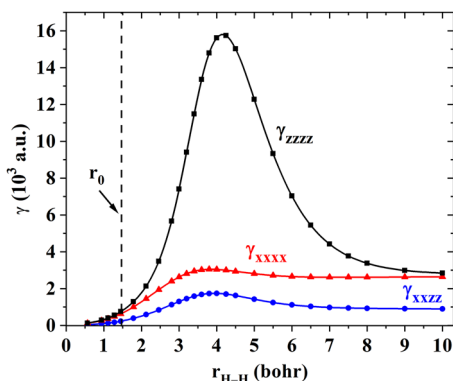


FIG. 3. CISD/D6Z results vs. the H–H distance for the different components of the  $\gamma$  tensor.

interpolations<sup>193</sup> of our results for  $\alpha_{zz}$  and Rychlewski's<sup>121</sup> range between  $-0.243\%$  and  $0.124\%$ . The average absolute value of the percent difference over the range of H–H distances from 0.6 a.u. to 10.0 a.u. is  $0.062\%$ . The polarizability components  $\alpha_{xx}$  and  $\alpha_{zz}$  have also been determined by Raj, Hamaguchi, and Witek,<sup>146</sup> using an aug-mcc-pV6Z basis with five additional sets of equally spaced bond functions. Their work focused on the frequency-dependent polarizability, but in addition, they provided values of the static polarizability for 61 H–H distances between 0.5 a.u. and 12.0 a.u.<sup>146</sup> Our results are also in very close agreement with the results of Raj *et al.* (see Fig. 6). Deviations between the Mathematica interpolations<sup>193</sup> of our results and the results of Raj *et al.*<sup>146</sup> for  $\alpha_{xx}$  range between  $0.029\%$  and  $0.145\%$ , with an average of  $0.071\%$ . For  $\alpha_{zz}$ , the deviations range between  $-0.039\%$  and  $0.054\%$ , with an average absolute difference of  $0.022\%$ . As shown in Fig. 7, our results for the interaction-induced changes in  $\alpha_{xx}$  approach the known long-range form quite closely as the H–H distance approaches 10 a.u. Our results for the interaction-induced changes in  $\alpha_{zz}$  are close to but slightly above the known long-range form at  $r = 10.0$  a.u. (see Fig. 7).

Values for the linear response tensors  $\mathbf{C}$  and  $\mathbf{E}$  are available in the literature only for  $r$  near equilibrium. Numerical comparisons have been made above.

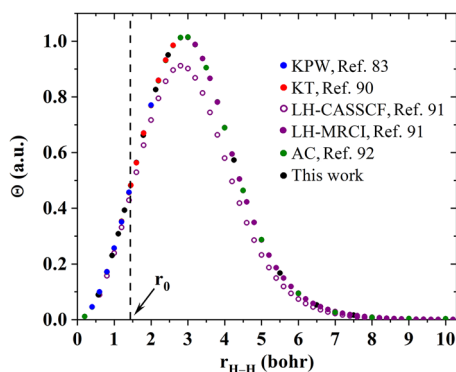


FIG. 4. Comparison with literature values of the quadrupole moment of  $\text{H}_2$  vs. the H–H distance in a.u. Except for the CASSCF values, the results are in very good agreement. A number of the points lie directly on top of each other so that not all points are apparent from the plot.

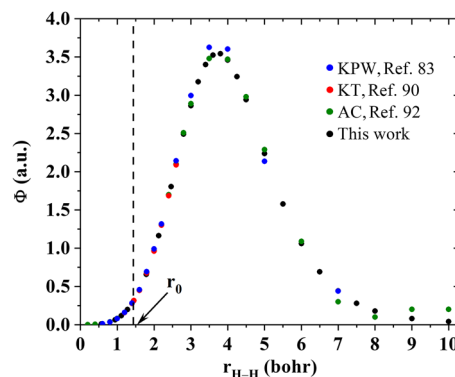


FIG. 5. Comparison with literature values of the hexadecapole moment of  $\text{H}_2$  vs. the H–H distance in a.u. A number of the points lie directly on top of each other so that not all points are apparent from the plot.

Berns and Wormer<sup>86</sup> have evaluated a nonlinear response function  $\beta_{211}^{mno}$  related to  $B_{\alpha,\beta,\gamma\delta}$  by  $B_{z,z,zz} = \beta_{211}^{000}$ ,  $B_{x,x,zz} = \beta_{211}^{011}$ ,  $B_{x,z,xz} = (3^{1/2}/2) \beta_{211}^{110}$ , and  $B_{x,x,xx} = (3^{1/2}/2) \beta_{211}^{211} - (1/2) \beta_{211}^{011}$ . They calculated  $\beta_{211}^{mno}$  for 34 H–H distances in the range from 0.2 a.u. to 6.0 a.u. Values of  $B_{z,z,zz}$ ,  $B_{x,x,zz}$ ,  $B_{x,z,xz}$ , and  $B_{x,x,xx}$  from the current calculation are compared with the results obtained by Berns and Wormer in Fig. 8. In general, the results agree very well in the range of  $r$  values from  $\sim 0.6$  a.u. to  $r \sim 2.5$  a.u.; for larger H–H distances, the results begin to diverge from each other. At  $r = 6.0$  a.u., the differences between the two sets of results are  $\sim 7\%$  for  $B_{x,x,xx}$ ,  $B_{x,x,zz}$ , and  $B_{x,z,xz}$  and a little over  $9\%$  for  $B_{z,z,zz}$ . The absolute values of our results are always larger than the earlier absolute values.

Berns and Wormer<sup>86</sup> have calculated the second hyperpolarizability  $\gamma$  out to  $r = 6.0$  a.u. Our results agree well with theirs over that range for each of the  $\gamma$  components, as shown in Fig. 9. Values for  $\gamma$  have also been obtained from 0.4 a.u. to 2.4 a.u. by Jaszuński and Roos<sup>123</sup> and Bishop and Pipin.<sup>125</sup> At  $r = 1.0$  a.u., our interpolated values of  $\gamma_{zzzz}$ ,  $\gamma_{xxxx}$ , and  $\gamma_{xxzz}$  are 322 a.u., 295 a.u., and 105 a.u., respectively, compared with 323 a.u., 287 a.u., and 108 a.u. from Ref. 123, with 314 a.u., 278 a.u., and 90 a.u. from Ref. 125, and with 324 a.u., 273 a.u., and 102 a.u. from Ref. 86. At  $r = 2.4$  a.u., our interpolated values of  $\gamma_{zzzz}$ ,  $\gamma_{xxxx}$ , and  $\gamma_{xxzz}$  are 3179 a.u., 1854 a.u., and 793 a.u., compared with 3183 a.u., 1799 a.u., and 837 a.u. from

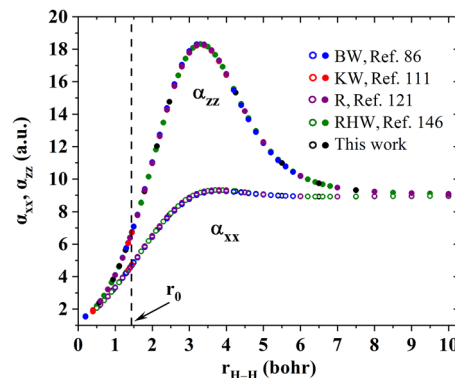


FIG. 6. Comparison with literature values of the dipole polarizabilities  $\alpha_{xx}$  (open circles) and  $\alpha_{zz}$  (solid circles) of  $\text{H}_2$  vs. the H–H distance in a.u. A number of the points lie directly on top of each other so that not all points are apparent from the plot.

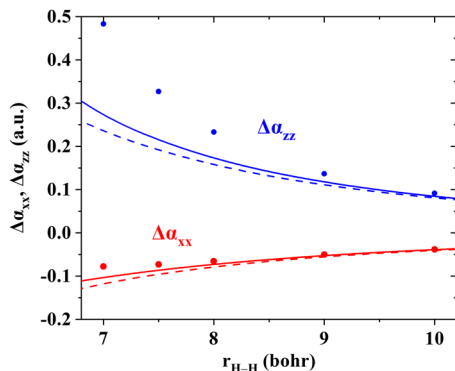


FIG. 7. Interaction-induced changes in polarizability  $\Delta\alpha_{xx}$  and  $\Delta\alpha_{zz}$  of  $H_2$  vs. the H–H distance  $r$  in a.u. at long range. The lines show the expected long-range behavior including dipole-induced-dipole (DID) interactions (dashed lines), which decay as  $r^{-3}$ , and DID plus higher order effects decaying as  $r^{-6}$  and  $r^{-8}$  (solid lines).<sup>46–48</sup>

Ref. 123, with 3137 a.u., 1793 a.u., and 754 a.u. from Ref. 125, and with 3145 a.u., 1769 a.u., and 764 a.u. from Ref. 86. For  $\gamma_{zzzz}$ , we typically find differences of  $\sim 0.5\%$  or less compared with values from Ref. 86 when  $r$  is less than or equal to 3.0 a.u., increasing to  $\sim 3.3\%$  at  $r = 6.0$  a.u. Discrepancies are somewhat larger in  $\gamma_{xxxx}$  ( $\sim 1.3\%$  near  $r_e$ ,  $\sim 5.3\%$  near 6.0 a.u.) and in  $\gamma_{xxzz}$  ( $\sim 4.1\%$  near  $r_e$ ,  $\sim 7.2\%$  near 6.0 a.u.), as shown in Fig. 9. In that figure, our results are also compared with values obtained by Bishop and Pipin.<sup>125</sup> In all cases, our values of the gamma hyperpolarizability are larger than the earlier values.

Bishop and Lam<sup>126</sup> have provided values of linear combinations of the  $\gamma$  tensor elements that are relevant for the Kerr effect and for electric-field second harmonic generation. In the static limit, only two of the linear combinations are independent,<sup>126</sup> so it is not possible to make a direct comparison with the individual values of  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xxzz}$ . However, we have used our values of  $\gamma$  to construct the linear combinations  $\gamma_{\parallel}^{\text{Kerr}}$  and  $\gamma_{\perp}^{\text{Kerr}}$  in the static limit, as functions of  $r$ . The results are compared with the work of Bishop and Lam<sup>126</sup> in Fig. S1 of the [supplementary material](#). For  $r < 4.0$  a.u., the results agree closely. At  $r = 4.0$  a.u., the values of  $\gamma_{\parallel}^{\text{Kerr}}$  and  $\gamma_{\perp}^{\text{Kerr}}$  obtained by Bishop and Lam<sup>126</sup> are  $\sim 2.4\%$  smaller than our

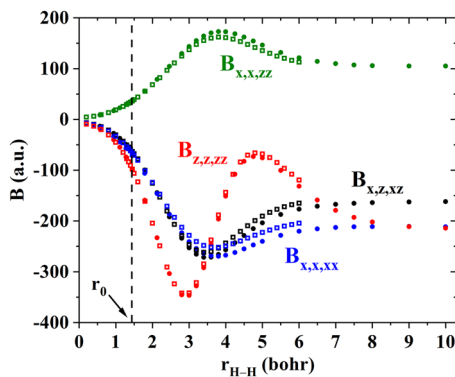


FIG. 8. Comparison with literature values of the dipole-dipole-quadrupole hyperpolarizability (B-tensor) components of  $H_2$  vs. the H–H distance in a.u. Solid circles correspond to this work, and open squares correspond to the work of Berns and Wormer (Ref. 86).

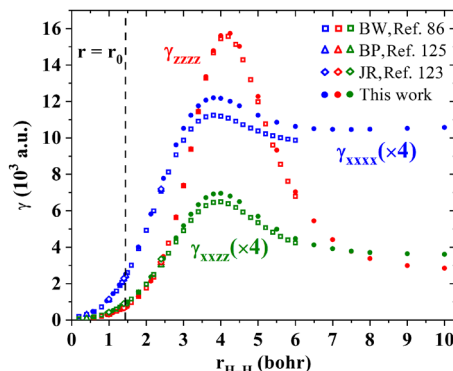


FIG. 9. Comparison with literature values of the second dipole hyperpolarizability ( $\gamma$ -tensor) components of  $H_2$  vs. the H–H distance in a.u.

values. From our results, the maxima in both  $\gamma_{\parallel}^{\text{Kerr}}$  and  $\gamma_{\perp}^{\text{Kerr}}$  occur close to  $r = 4.0$  a.u.

## V. LONG-RANGE ANALYSIS AND APPLICATIONS

When the two H nuclei are widely separated, the electrical properties are determined by the properties of individual H atoms, as modified by classical induction and van der Waals dispersion interactions. For an isolated H atom,  $\Theta$ ,  $\Phi$ , and  $E$  vanish, due to spherical symmetry. With the D6Z basis for the H atom, we obtained polarizabilities  $\sim 0.16\%$  different from the exact results,  $\alpha_{xx} = \alpha_{zz} = 9/2$  a.u. The B tensor of an atom in an S state has the form<sup>49</sup>

$$B_{\alpha\beta,\gamma\delta} = (B/4) \left[ 3(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - 2\delta_{\alpha\beta} \delta_{\gamma\delta} \right]. \quad (21)$$

For the H atom,  $B = -213/2 = -106.5$  a.u. With the D6Z basis, we obtained  $B_{x,x,xx} = B_{z,z,zz} = -106.86$  a.u., an error of  $\sim 0.34\%$ . The C tensor of an atom in an S state has the form<sup>4</sup>

$$C_{\alpha\beta,\gamma\delta} = C_0 \left[ (1/2)(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - (1/3)\delta_{\alpha\beta} \delta_{\gamma\delta} \right], \quad (22)$$

where  $C_0 = 15/2 = 7.5$  a.u. for the H atom. With the D6Z basis, we find that  $C_{xx,xx} = C_{zz,zz} = (4/3) C_{xz,xz} = 4.9813$  a.u. or  $C_0 = 7.472$  a.u., an error of  $0.37\%$ . Note that  $C_0 = (3/2) C$  in the notation of Bishop and Pipin.<sup>194</sup> The static  $\gamma$  hyperpolarizability is symmetric in all indices, so for an atom in an S state,

$$\gamma_{\alpha\beta\gamma\delta} = (\gamma/3) (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \quad (23)$$

and for the H atom,  $\gamma = 10\,665/8 = 1333.125$  a.u. Our *ab initio* calculations with the D6Z basis give  $\gamma_{xxxx} = \gamma_{zzzz} = 1342$  a.u., an error of  $\sim 0.67\%$ .

From Fig. 1, it is apparent that  $\Theta$  and  $\Phi$  tend to zero as the H–H distance increases, while  $\alpha_{xx}$  and  $\alpha_{zz}$  both converge toward twice the H atom polarizability. One-third of the trace of the polarizability tensor is 8.9905 at  $r = 10.0$  a.u., which differs from the true long-range limit by  $0.106\%$ . At that same H–H distance, the average of  $\gamma_{xxxx}$ ,  $\gamma_{yyyy}$ , and  $\gamma_{zzzz}$  is 2708 a.u., which differs from twice the actual H-atom value of 2666.25 a.u. by  $\sim 1.57\%$ . The value of  $\gamma_{xxzz}$  at  $r = 10.0$  a.u. differs from twice the H-atom value by  $\sim 1.38\%$ . At  $r = 10.0$  a.u., our values of  $B_{x,x,xx}$  and  $B_{z,z,zz}$  differ from twice the isolated-atom

values by  $\sim 0.73\%$  and  $\sim 0.52\%$ , respectively. Similarly, our results for  $B_{x,x,zz}$  and  $B_{x,z,xz}$  at  $r = 10.0$  a.u. come quite close to twice the isolated-atom values, with errors of 1.40% and 1.41%, respectively.

The components of  $C$  and  $E$  diverge in the long-range limit, as a consequence of the origin-dependence of the

multipole operators, their expectation values, and the susceptibilities. If the axis systems (1) and (2) are related by translation so that  $r_\alpha^{(2)} = r_\alpha^{(1)} - R_\alpha$ , where  $R_\alpha$  denotes the coordinates ( $X$ ,  $Y$ , and  $Z$ ) of the origin of the translated coordinate system (2) in the original system (1), then the components of the  $C$  and  $E$  tensors generally transform as<sup>5</sup>

$$C_{xx,xx}^{(2)} = C_{xx,xx}^{(1)} - (4/3)A_{x,xx}^{(1)}X + (2/3)A_{y,xx}^{(1)}Y + (2/3)A_{z,xx}^{(1)}Z + (4/3)\alpha_{xx}^{(1)}X^2 + (1/3)\alpha_{yy}^{(1)}Y^2 + (1/3)\alpha_{zz}^{(1)}Z^2 - (4/3)\alpha_{xy}^{(1)}XY + (2/3)\alpha_{yz}^{(1)}YZ - (4/3)\alpha_{zx}^{(1)}ZX, \quad (24)$$

$$C_{zz,zz}^{(2)} = C_{zz,zz}^{(1)} - (4/3)A_{z,zz}^{(1)}Z + (2/3)A_{y,zz}^{(1)}Y + (2/3)A_{x,zz}^{(1)}X + (4/3)\alpha_{zz}^{(1)}Z^2 + (1/3)\alpha_{yy}^{(1)}Y^2 + (1/3)\alpha_{xx}^{(1)}X^2 - (4/3)\alpha_{zy}^{(1)}YZ + (2/3)\alpha_{yx}^{(1)}XY - (4/3)\alpha_{xz}^{(1)}XZ, \quad (25)$$

$$C_{xz,xz}^{(2)} = C_{xz,xz}^{(1)} - A_{z,xz}^{(1)}X - (2/3)A_{x,xz}^{(1)}Z + (3/4)\alpha_{zz}^{(1)}X^2 + (3/4)\alpha_{xx}^{(1)}Z^2 + (3/2)\alpha_{xz}^{(1)}XZ, \quad (26)$$

$$E_{x,xxx}^{(2)} = E_{x,xxx}^{(1)} - 3A_{x,xx}^{(1)}X + 2A_{x,xy}^{(1)}Y + 2A_{x,xz}^{(1)}Z + \alpha_{xx}^{(1)}[3X^2 - (3/2)Y^2 - (3/2)Z^2] - 3\alpha_{xy}^{(1)}XY - 3\alpha_{xz}^{(1)}XZ, \quad (27)$$

$$E_{z,zzz}^{(2)} = E_{z,zzz}^{(1)} - 3A_{z,zz}^{(1)}Z + 2A_{z,zy}^{(1)}Y + 2A_{z,zx}^{(1)}X + \alpha_{zz}^{(1)}[3Z^2 - (3/2)X^2 - (3/2)Y^2] - 3\alpha_{yz}^{(1)}YZ - 3\alpha_{zx}^{(1)}XZ, \quad (28)$$

where  $A_{\alpha,\beta\gamma}$  denotes the dipole-quadrupole polarizability. The two hydrogen nuclei are located at  $(0, 0, -r/2)$  and  $(0, 0, r/2)$ . At very large separations, in the reference frames of the individual hydrogen nuclei, the  $C$  tensor of each is given by Eq. (22), the polarizabilities are isotropic, and both the  $E$  and  $A$  tensors vanish. Converting the tensor values for each H atom separately to the center of mass as the origin, we obtain the expected long-range behavior of the tensors for the H–H pair (in a.u.),

$$C_{xx,xx} \rightarrow 2C_{xx,xx}^H + (1/6)\alpha^H r^2 = 10 + (3/4)r^2, \quad (29)$$

$$C_{zz,zz} \rightarrow 2C_{zz,zz}^H + (2/3)\alpha^H r^2 = 10 + 3r^2, \quad (30)$$

$$C_{xz,xz} \rightarrow 2C_{xz,xz}^H + (3/8)\alpha^H r^2 = 15/2 + (27/16)r^2, \quad (31)$$

$$E_{x,xxx} \rightarrow -(3/4)\alpha^H r^2 = -(27/8)r^2, \quad (32)$$

$$E_{z,zzz} \rightarrow (3/2)\alpha^H r^2 = (27/4)r^2. \quad (33)$$

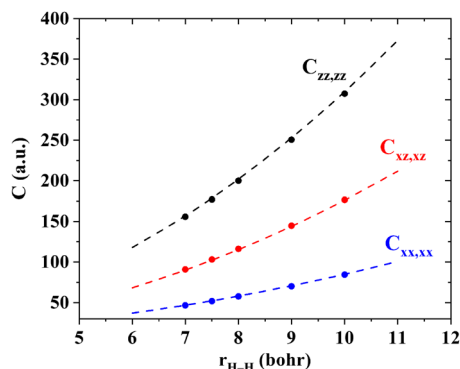


FIG. 10. Calculated  $C_{xx,xx}$ ,  $C_{zz,zz}$ , and  $C_{xz,xz}$  values compared to the long-range predictions (dashed lines).

In Fig. 10, the *ab initio* values of  $C_{xx,xx}$ ,  $C_{zz,zz}$ , and  $C_{xz,xz}$  are compared with the long-range forms in Eqs. (29)–(31), for  $r$  from 7.0 to 10.0 a.u. It is evident that the  $C$  tensor has taken on its long-range limiting form at these H–H distances. In Fig. 11,  $E_{z,zzz}$  is compared with its long-range limiting form from Eq. (33) and also with  $(-2)E_{x,xxx}$ . Again, the predictions of the long-range model are excellent, for  $r$  from 7.0 to 10.0 a.u.

In order to evaluate the rovibrational matrix elements of the electrical moments and susceptibilities of  $H_2$ , we have solved the rovibrational Schrödinger equation for all of the bound vibrational levels of  $H_2$  ( $v = 0-14$ ) by the Numerov-Cooley method,<sup>195,196</sup> with rotational quantum numbers  $J = 0-3$ . The grid for the numerical work consisted of 10 000 points between  $r = 0.58$  a.u. and  $r = 9.8$  a.u., to obtain the bound  $\chi_{v,J}(r)$  wave functions. Then we obtained the rovibrational average of each property  $P$  in state  $(v, J)$  as the matrix

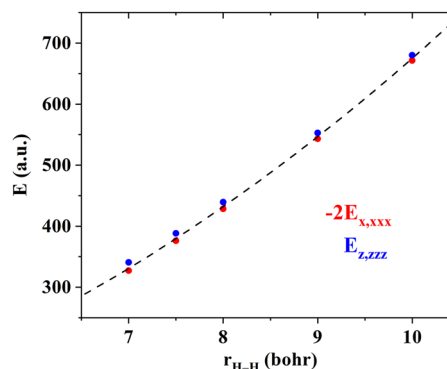


FIG. 11. Calculated  $E_{x,xxx}$  and  $E_{z,zzz}$  values compared to the long-range predictions (dashed line).

element  $\langle \chi_{v,J}(r) | P(r) | \chi_{v,J}(r) \rangle$ . In Table V, we list our results for the expectation values of  $\Theta$ ,  $\Phi$ ,  $\alpha_{xx}$ , and  $\alpha_{zz}$  in vibrational states  $v$  from 0 to 5, for  $J = 0$ . The full numerical results for  $v = 0-14$  and  $J = 0-3$  are given in the [supplementary material](#). Generally, the results compare well with the expectation values in the literature. The expectation value  $\langle \chi_{0,0}(r) | \Theta(r) | \chi_{0,0}(r) \rangle = 0.4828$  a.u. that we obtained for the quadrupole in the ground vibrational state is within the range of the previous theoretical values, from 0.48258 to 0.4842(4) a.u. (see references in the footnotes of Table V), but it is slightly smaller than average. The same trend is observed for the other expectation values. For the expectation value of the quadrupole in the state with  $v = 0$  and  $J = 1$ , we find 0.4840 a.u., compared with the experimental result of 0.4853 a.u.<sup>197</sup>

In Table VI, we list the vibrational averages of the independent elements of  $B$ ,  $C$ ,  $E$ , and  $\gamma$  for vibrational quantum numbers  $v = 0$  to 5 and  $J = 0$ . As before, the full numerical results for  $v = 0-14$  and  $J = 0-3$  are given in the [supplementary material](#). In Tables V and VI, we also compare the expectation value of each of the properties in the ground

TABLE V. CISD/D6Z rovibrationally averaged values (in a.u.) for  $\Theta$ ,  $\Phi$ , and  $\alpha$  tensors for  $v = 0-5$  and  $J = 0$ .

$v$	$\Theta$	$\Phi$	$\alpha_{xx}$	$\alpha_{zz}$
$r = r_0^a$	0.4823	0.3139	4.7308	6.7178
0	0.4828	0.3320	4.7336	6.7710
	0.460(21) <sup>b</sup>	0.33282 <sup>c</sup>	4.7293 <sup>d</sup>	6.7632 <sup>d</sup>
	0.4853 <sup>e</sup>	0.3328 <sup>f</sup>	4.72943 <sup>g</sup>	6.73543 <sup>g</sup>
	0.48354 <sup>h</sup>	0.3362(7) <sup>i</sup>	4.74057 <sup>j</sup>	6.76999 <sup>j</sup>
	0.483103 <sup>c</sup>	0.338(3) <sup>k</sup>	4.7392 <sup>l</sup>	6.7630 <sup>l</sup>
	0.483103 <sup>f</sup>			
	0.48258 <sup>m</sup>			
	0.4833(4) <sup>i</sup>			
	0.4842(4) <sup>k</sup>			
1	0.5344	0.4535	5.0501	7.5518
	0.53515 <sup>h</sup>	0.45453 <sup>c</sup>	5.0559 <sup>d</sup>	7.5421 <sup>d</sup>
	0.534664 <sup>c</sup>	0.458(2) <sup>i</sup>	5.05750 <sup>j</sup>	7.54993 <sup>j</sup>
	0.5351(3) <sup>i</sup>			
2	0.5829	0.5914	5.3568	8.3473
	0.58610 <sup>h</sup>	0.59720 <sup>c</sup>	5.37821 <sup>j</sup>	8.37631 <sup>j</sup>
	0.585513 <sup>c</sup>	0.601(2) <sup>i</sup>		
	0.5855(3) <sup>i</sup>			
3	0.6331	0.7560	5.6853	9.2227
	0.63540 <sup>h</sup>	0.767(3) <sup>i</sup>	5.70162 <sup>j</sup>	9.24215 <sup>j</sup>
	0.6346(3) <sup>i</sup>			
4	0.6840	0.9514	6.0361	10.1774
	0.68200 <sup>h</sup>		6.02581 <sup>j</sup>	10.13674 <sup>j</sup>
5	0.7307	1.1713	6.3852	11.1467
	0.72475 <sup>h</sup>		6.34904 <sup>j</sup>	11.04514 <sup>j</sup>

<sup>a</sup>Values at  $r_0 = 1.449$  a.u.

<sup>b</sup>Reference 84: derived from experimental data.

<sup>c</sup>Reference 90.

<sup>d</sup>Reference 111.

<sup>e</sup>Reference 197: experimental value for  $v = 0$ ,  $J = 1$ .

<sup>f</sup>Reference 72.

<sup>g</sup>Reference 115.

<sup>h</sup>Reference 94.

<sup>i</sup>Reference 92.

<sup>j</sup>Reference 121.

<sup>k</sup>Reference 93.

<sup>l</sup>Reference 95.

<sup>m</sup>Reference 71: CCSD/D5Z.

vibrational state with the value at the vibrationally averaged bond length  $r_0$  in the ground vibrational state. For  $\alpha_{xx}$  and  $\Theta$ , the differences are 0.06% and 0.10%, respectively. For  $\alpha_{zz}$ , the difference is 0.79%. For the components of the C and B tensors, the difference is typically between 1% and 2%, while for the components of  $\gamma$ , the differences fall between 2% and 3%. The largest differences are found for  $\Phi$  (5.45%),  $E_{x,xxx}$  (5.06%), and  $E_{z,zzz}$  (6.35%). For all of the properties, however, the value at  $r_0$  provides a reasonable estimate of the vibrational average.

The moments and susceptibilities computed in this work are useful for computational work in collision-induced spectroscopy. Collision-induced dipoles  $\Delta\mu$  and polarizabilities  $\Delta\alpha$  obtained from *ab initio* calculations can be tested in part by examining whether they converge to the known long-range functional forms, as the separation  $R$  between collision partners increases. For  $H_2$  interacting with a collision partner such as H,<sup>23,24</sup> inert gas atoms,<sup>25-45</sup>  $H_2$ ,<sup>12-22</sup> or other diatomics, the properties evaluated in this work permit such tests over a wide range of H-H distances.

For an  $H_2-H_2$  pair,  $\alpha$ ,  $\Theta$ ,  $\Phi$ , and  $E$  determine the classical induction effects on  $\Delta\mu$  through order  $R^{-7}$  (Refs. 81, 198, and 199). The dispersion effects through order  $R^{-7}$  depend on integrals that contain  $\alpha(i\omega)$  and  $B(0, i\omega)$  at imaginary frequencies,<sup>51,174-179</sup> but they can be approximated from the static  $\alpha$  and  $B$  values and dispersion energy coefficients,<sup>81</sup> for H-H distances where  $\alpha(i\omega)$  and  $B(0, i\omega)$  are not yet available. The isotropic polarizability and the quadrupole give the leading quadrupolar induction contribution to  $\Delta\mu$ , which varies as  $R^{-4}$  (Ref. 198). Quadrupolar induction makes the dominant contribution to the intensity of rotational transitions with  $\Delta J = \pm 2$  on one  $H_2$  molecule and  $\Delta J = 0$  on the other; it accounts for the majority of the collision-induced absorption intensity, except in the far wings of the absorption spectra.<sup>9-11,200</sup> Similarly, the isotropic polarizability and the hexadecapole moment give the leading classical induction contribution (of order  $R^{-6}$ ) to the intensity of rotational transitions with  $\Delta J = \pm 4$  on one  $H_2$  molecule and  $\Delta J = 0$  on the other.<sup>81</sup> The anisotropy of the polarizability, the quadrupole, and the second-rank component of the  $E$  tensor contribute to the intensity of double rotational transitions with  $\Delta J = \pm 2$  on both molecules.<sup>81</sup> Double transitions with  $\Delta J$  up to  $\pm 4$  on one molecule and  $\Delta J = \pm 2$  on the other may occur due to the anisotropic polarization of one molecule by the hexadecapolar field of the other and the response via the fourth-rank component of  $E$  to the non-uniformity of the quadrupole field gradient.<sup>81</sup> The anisotropy of the potential also contributes to transitions with higher  $\Delta J$  and the lower-order classical induction mechanisms.<sup>9-11</sup> Second-order induction effects on  $\Delta\mu$  tend to be smaller since they vary as  $R^{-7}$  in the separation between the molecules, but they are determined by the polarizability tensor components and the quadrupole moment.<sup>81</sup> For atoms interacting with  $H_2$ , values for  $\alpha$ ,  $\Theta$ , and  $\Phi$  of  $H_2$  are needed to determine the classical induction contributions to  $\Delta\mu$ .<sup>80</sup> The  $B$  tensor is needed (in addition to  $\alpha$  and the van der Waals energy coefficients) to estimate the van der Waals dispersion dipole.<sup>80</sup> The  $E$  tensor is needed for  $\Delta\mu$  of diatomic molecules interacting with diatomics,<sup>81</sup> but not for the terms through order  $R^{-7}$  in  $\Delta\mu$  for atom-diatom molecule interactions.



TABLE VI. CISD/D6Z rovibrationally averaged values (in a.u.) for E, C, B, and  $\gamma$  tensors for  $v = 0-5$  and  $J = 0$ .

$v$	$E_{x,xxx}$	$E_{z,zzz}$	$C_{xx,xx}$	$C_{zz,zz}$	$C_{xz,xz}$	$B_{x,x,xx}$	$B_{z,z,zz}$	$B_{x,x,zz}$	$B_{x,z,xz}$	$\gamma_{xxxx}$	$\gamma_{zzzz}$	$\gamma_{xxzz}$
$r = r_0$	-1.7738	4.4792	5.198	6.397	4.447	-71.49	-98.05	36.82	-63.57	628	750	231
0	-1.8683	4.7828	5.246	6.518	4.512	-72.37	-100.24	37.37	-64.76	641	773	237
1	-2.5117	6.6840	5.914	7.660	5.211	-83.32	-120.27	43.47	-76.57	763	961	289
2	-3.2758	9.0004	6.611	8.932	5.968	-94.62	-141.16	49.92	-89.04	890	1185	345
3	-4.2376	11.9664	7.402	10.462	6.855	-107.19	-164.09	57.27	-103.11	1034	1476	412
4	-5.4555	15.7660	8.305	12.318	7.905	-121.12	-188.50	65.64	-118.88	1196	1863	491
5	-6.9523	20.4599	9.289	14.495	9.100	-135.67	-211.96	74.71	-135.43	1369	2372	581

Intensities of isotropic collision-induced Rayleigh and rototranslational Raman light scattering depend on the scalar component  $\Delta\alpha_0^0$  of the interaction-induced change in the polarizability of the collision partners.<sup>10,11</sup> Intensities of depolarized rototranslational Raman scattering depend on the second-rank tensor components  $\Delta\alpha_2^M$  of the interaction-induced change in the polarizability.<sup>10,11</sup> For interactions between diatomic molecules, the classical induction effects in both  $\Delta\alpha_0^0$  and  $\Delta\alpha_2^M$  depend on  $\alpha$ , E, and B;<sup>201-207</sup> static values of  $\alpha$  and  $\gamma$  are needed along with dispersion energy coefficients to estimate the van der Waals dispersion contributions to  $\Delta\alpha_0^0$  and  $\Delta\alpha_2^M$ .<sup>208-210</sup> The E-tensor mechanism is the only one that gives rise to transitions with  $\Delta J = \pm 4$  in the isotropic light scattering spectra of homonuclear diatomic molecules, through order  $R^{-6}$  (Ref. 206). The same tensors are needed for the classical induction and dispersion contributions to collision-induced light scattering intensities from atoms interacting with diatomic molecules.<sup>211</sup>

## VI. SUMMARY

We have completed a systematic study of the moments and static susceptibilities of the hydrogen molecule, using the large correlation-consistent basis set d-aug-cc-pV6Z and full configuration interaction wave functions. We have tested the results by repeating the calculations with 6s 6p 6d 3f 1g 1h mid-bond functions added to the d-aug-cc-pV6Z basis. Our results for the leading charge moments  $\Theta$  and  $\Phi$  and the independent components of the linear response tensors  $\alpha$ , E, and C are listed in Table III for the full range of H-H separations investigated here, 0.567 a.u. to 10.0 a.u. The independent components of the hyperpolarizabilities B and  $\gamma$  are listed in Table IV. In general, our results agree well with earlier, highly accurate calculations for the H-H separations treated in common: For  $\alpha_{xx}$ , we find an average difference between the Mathematica interpolations of our values and Rychlewski's<sup>121</sup> of 0.093% and a smaller difference of 0.071% with the values of Raj *et al.*<sup>146</sup> For  $\alpha_{zz}$ , the average absolute value of the difference is even smaller, 0.062% vs. Ref. 121 and 0.022% vs. Ref. 146. Differences from earlier results are most noticeable for the B tensor components  $B_{x,x,xx}$  and  $B_{x,z,xz}$  and for the hyperpolarizability component  $\gamma_{xxxx}$  in the range of  $r$  values from  $\sim 3.0$  a.u. out to 6.0 a.u., where the earlier calculations ended. We have provided the first accurate *ab initio* results for  $\Theta$  and  $\Phi$  for  $r > 7.0$  a.u., for B and  $\gamma$  for  $r > 6.0$  a.u., and for C and E for any separations  $r$  outside a narrow range around the potential minimum. We have also demonstrated that the components of

$\alpha$ , B, and  $\gamma$  approach twice the single-atom values as the separation  $r$  between the nuclei increases; so those properties are size-consistent in this treatment. The quadrupole  $\Theta$  and hexadecapole  $\Phi$  tend to zero as  $r$  increases, as expected. We have proven that the quadrupole-polarizability C and the dipole-octopole polarizability E diverge as the separation between the nuclei increases. In Tables S4-S6, we have provided the expectation values of the moments and susceptibilities for all of the bound vibrational levels of  $H_2$  (i.e., up to vibrational quantum number  $v = 14$ ) and rotational quantum numbers  $J = 0-3$ . The expectation values in the ground vibrational and rotational state generally compare well with the values at the vibrationally averaged bond length  $r_0$ . The differences are largest (at  $\sim 5\%-7\%$ ) for  $\Phi$  and E,  $\sim 1\%-3\%$  for C, B, and  $\gamma$ , and less than 1% for  $\Theta$  and  $\alpha$  (in fact, substantially less than 1% for  $\Theta$  and  $\alpha_{xx}$ ).

The moments and susceptibilities of  $H_2$  given in this work determine long-range induction effects on dipole moments and polarizabilities, for an  $H_2$  molecule with a variable H-H separation colliding with another  $H_2$  molecule, an H atom, or an inert gas atom. In combination with the dispersion energy coefficients, the results will yield an estimate of the van der Waals dispersion terms in  $\Delta\mu$  and  $\Delta\alpha$ . The results permit a useful test of *ab initio* calculations of collision-induced properties that are used to model collision-induced absorption spectra and interaction-induced Rayleigh and Raman light scattering spectra. For well-separated pairs of molecules, the *ab initio* results should converge to the known long-range functional forms (which depend on the properties given in this work). The results of this work are sufficient to generate vibrational transition matrix elements of properties between moderately high vibrational states (up to  $v = 8$ ), as needed for astrophysical modeling of the radiative profiles of cool white dwarf stars.<sup>9,212-220</sup>

## SUPPLEMENTARY MATERIAL

The supplementary material includes a plot of the Kerr coefficients  $\gamma_{\parallel}^{\text{Kerr}}$  and  $\gamma_{\perp}^{\text{Kerr}}$  in the static limit as functions of the H-H separation  $r$  from this work, compared with the results of Bishop and Lam.<sup>126</sup> A brief summary of the molecular beam method used by Nelissen, Reuss, and Dymanus to determine the polarizability anisotropy is also provided.<sup>107</sup> Table S1 lists the values of the energy,  $\Theta$ ,  $\Phi$ ,  $\alpha_{xx}$ ,  $\alpha_{zz}$ ,  $E_{x,xxx}$ ,  $E_{z,zzz}$ ,  $C_{xx,xx}$ ,  $C_{zz,zz}$ , and  $C_{xz,xz}$  for  $H_2$  obtained with the d-aug-cc-pV6Z basis, augmented by 6s 6p 6d 3f 1g 1h mid-bond functions<sup>190,191</sup> for 17 values of  $r$  between 1.787 a.u. and 7.000

a.u. Over the same range of  $r$  values and with the same basis (including the mid-bond functions), values of  $B_{x,x,xx}$ ,  $B_{z,z,zz}$ ,  $B_{x,x,zz}$ ,  $B_{x,z,xz}$ ,  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xzxz}$  are listed in Table S2. Table S3 lists the values of the energy of  $H_2$  at  $r_0$  and  $r_e$  and compares with literature values for the minimum of the potential. The energies and expectation values of  $\Theta$ ,  $\Phi$ ,  $\alpha_{xx}$ ,  $\alpha_{zz}$ ,  $E_{x,xxx}$ , and  $E_{z,zzz}$  are listed in Table S4 for the full range of vibrational quantum numbers  $v = 0-14$ , with rotational quantum numbers  $J = 0-3$ . Table S5 lists the expectation values of  $C_{zz,zz}$ ,  $C_{xx,xx}$ ,  $C_{xz,xz}$ ,  $B_{x,z,xz}$ ,  $B_{x,x,zz}$ ,  $B_{x,x,xx}$ , and  $B_{z,z,zz}$  for the same range of rovibrational states,  $v = 0-14$ ,  $J = 0-3$ . Table S6 similarly lists the expectation values of the independent components of  $\gamma$ ,  $\gamma_{xxxx}$ ,  $\gamma_{zzzz}$ , and  $\gamma_{xzxz}$ . The h2.zip file contains separate files for the rovibrational wave functions of each ( $v$ ,  $J$ ) pair.

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