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REGULAR ARTICLE

NMR shielding constants in hydrogen molecule isotopomers

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Abstract We analyze the NMR shielding constants in three isotopomers of the hydrogen molecule: H_2, HD and D_2. The results obtained within the Born–Oppenheimer approximation using the coupled-cluster singles-and-doubles model are very close to the previous theoretical values. In particular, the isotope shifts computed using significantly larger basis sets agree with the earlier literature results, confirming the disagreement of these calculations with the available experimental data. To examine the accuracy of the computed isotope shifts, we analyze in addition the relativistic corrections and estimate the role of the adiabatic and nonadiabatic effects. The relativistic corrections appear to be negligible; on the other hand, the changes in the shielding constants due to the adiabatic and nonadiabatic effects may account for the discrepancies between the computed and experimental isotope shifts.

Keywords Shielding constants · Isotope shifts · Hydrogen molecule · CCSD calculations

1 Introduction

The NMR shielding constant in hydrogen molecule was studied more than ten years ago in a series of papers by Sundholm et al. [1–3]. In these benchmark calculations, the authors applied the CCSD method, which is for the two-electron hydrogen molecule equivalent to the full configuration interaction (FCI) approach; therefore, within the nonrelativistic Born–Oppenheimer approximation, the error in the results is only due to the incompleteness of the basis set. They have studied convergence of the results with the extension of the basis set, and to ensure gauge-origin invariant results used London atomic orbitals [4] in all the shielding calculations. The dependence of the shielding on internuclear distance was analyzed, and to make a direct comparison of the results with experiment rovibrational averaging was performed. This enabled the description of the temperature dependence of the shielding and an analysis of the isotope shifts. The computed isotope shifts may be directly compared to experimental data, in contrast to the computed shielding constants.

We begin following precisely the same approach; we use the CCSD method and London atomic orbitals. The improvements and speed-up of the calculations allow presently the use of significantly larger basis sets, thus our values should be closer to the basis set limit and provide improved estimates of the accuracy of the results obtained within the Born–Oppenheimer approximation. Next, we analyze the rovibrational effects and the temperature dependence of the shielding constants and isotope shifts. In addition, we discuss the role of the adiabatic corrections

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Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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and nonadiabatic effects on the shielding and we consider the relativistic effects. It appears that various contributions to the shielding constants in the hydrogen molecule can now be estimated with higher precision than it was previously done. Although the overall changes in the computed shielding constants for each isotopomer are small, they affect noticeably the computed isotope shifts. Moreover, these isotope shifts can be estimated with higher accuracy than the shielding constants, due to systematic cancellation of some of the unknown contributions.

2 CCSD shielding curve: basis set dependence

In the nonrelativistic approach using the Born–Oppenheimer approximation, the description of the shielding curve, together with the potential curve, determines the results. As mentioned, at the CCSD level, the accuracy depends only on the choice of the basis set. We begin using the same basis sets for the potential curve and for the property curve.

All the quoted below results of Sundholm et al. [1–3] have been obtained in the "B" basis set, which included [8s4p3d2f] uncontracted Gaussian-type functions. We present results for two significantly larger basis sets, called a6Zus and a7Zus in what follows. The smaller one is the aug-pV6Z basis [5] with all the [11s6p5d4f3g2h] orbitals (including the s-type functions) uncontracted. The larger aug-pV7Z basis [5] is [15s7p6d5f4g3h2i], with all the orbitals uncontracted. In all the CCSD calculations, we use spherical harmonic functions, thus there are 262 functions in the smaller and 392 functions in the larger basis set.

The results for selected internuclear distances are shown in Table 1. At $R = 1.4\ a_0$, close to the equilibrium distance, the a6Zus/a7Zus difference in the shielding is below 0.0005 ppm for individual components, and it is much smaller for the isotropic shielding, -0.000032 ppm. These results are in agreement with the results and the trends observed in [1]: the [8s4p3d2f] values at $R = 1.4\ a_0$ were $\sigma = 26.680$ and $\Delta\sigma = 1.815$ ppm, with the average becoming smaller and the anisotropy increasing with the basis set extensions. The basis set error was estimated in [1] as 0.02 ppm, in fact the difference between 26.680 ppm and our best result is much smaller, only -0.003 ppm. From the discussed above differences between a6Zus and a7Zus shielding tensor components, it appears that the remaining basis set error in the isotropic shielding is now below 0.0005 ppm.

For large internuclear distances the shielding of the nucleus should be close to the shielding constant in an isolated atom. The nonrelativistic shielding constant for the hydrogen atom is easily obtained; since only the diamagnetic term contributes it can be calculated as the expectation value $\sigma^{\text{dia}} = \alpha^2 \langle r_{iK}{}^{-1} \rangle / 3 = 17.750454$ ppm, where α is the fine structure constant and r_{iK} is the electron-nucleus distance. As shown by the tabulated results, the basis sets we use enable convergence to the correct asymptotic limit at large internuclear distances.

Table 1 Basis set dependence of the shielding tensor

R	σ	$\Delta\sigma$	$\sigma_\perp$	$\sigma_\parallel$
a6Zus				
1.2	29.080110	2.013818	28.408837	30.422655
1.4	26.677143	1.824096	26.069111	27.893207
2.0	21.989338	1.185004	21.594337	22.779341
15.0	17.750353	0.023671	17.742463	17.766134
20.0	17.750388	0.009986	17.747059	17.757045
a7Zus				
1.2	29.080111	2.014570	28.408588	30.423158
1.4	26.677111	1.824785	26.068849	27.893634
2.0	21.989305	1.185452	21.594154	22.779606
15.0	17.750404	0.023671	17.742514	17.766185
20.0	17.750437	0.009986	17.747108	17.757094

R in a_0, σ, $\Delta\sigma$, $\sigma_\perp$ and $\sigma_\parallel$ in ppm

3 Shielding and shielding derivatives at the potential minimum

To describe the dependence of molecular properties on the internuclear distance in the equilibrium region of a diatomic molecule one can use the expansion

$$\sigma(x) = \sigma_e^{(0)} + \sigma_e^{(1)}x + \sigma_e^{(2)}x^2 + \cdots \qquad (1)$$

where $x = (R - R_e)/R_e$. For the isotropic shielding, the results, shown in Table 2, are much closer to the previously calculated values of [2] than to the data extracted from experiment. In particular, the value of $\sigma_e^{(1)}$—the first shielding derivative at equilibrium—extracted from the

Table 2 Isotropic nuclear magnetic shielding function

	R_e	$\sigma_e^{(0)}$	$\sigma_e^{(1)}$	$\sigma_e^{(2)}$
a7Zus	1.40117057	26.664609	−14.95184	11.900
a6Zus	1.40122487	26.664064	−14.95176	11.890
Ref. [2][a]	1.40124	26.6668[b]	−14.935	11.696
Exp.[c]	1.40125	26.689 (3)	−15.1885	9.8426
Exp.[d]	1.40125		−8.974 (47)	

R_e in a_0, $\sigma_e^{(0)}$, $\sigma_e^{(1)}$, $\sigma_e^{(2)}$ in ppm

[a] Ref. [2], Basis set B. The corresponding value obtained from the explicitly correlated wavefunction potential (see below) is 1.401085 a_0

[b] Ref. [3]; Given as 26.667 ppm in [2]

[c] Ref. [6], Obtained from spin-rotation data

[d] Ref. [6], Based partly on the experimental isotope shifts of [7]

isotope shifts differs significantly from all the other results. For the anisotropy, $\Delta\sigma_e^{(0)}$ we find with the a6Zus and a7Zus basis sets 1.822837 and 1.823585 ppm, to be compared with 1.814 ppm in [2].

We do not repeat the detailed analysis of spin-rotation constants given in [3], we only present for comparison some results obtained with the a7Zus basis at $R = 1.40124$ a_0, the equilibrium distance of [3]. For the spin-rotation constant in H_2 we obtain 115.5452 kHz (115.468 kHz in [3], derived using experimental data). The total calculated shielding at this geometry is 26.663869 ppm, to be compared with 26.6668 ppm in [3].

4 Relativistic corrections

To estimate the relativistic correction, we compare the shielding at 1.4 a_0 calculated at the restricted Hartree-Fock (RHF) level with the corresponding Dirac–Hartree–Fock (DHF) value. In the RHF calculation, we used the pV6Z [10s5p4d3f2g1h/6s5p4d3f2g1h] set, with Cartesian basis functions. In the DHF calculation, this constituted the large component of the basis, the small component was generated using the unrestricted kinetic balance approach. Both in RHF and in DHF, we applied London orbitals to ensure gauge invariance of the results. This is particularly important because even for significantly larger but standard basis sets the differences in the shielding between the nucleus chosen as the gauge origin and the other one are much larger than the required relativistic corrections, making the RHF/DHF comparison meaningless.

The results are shown in Table 3. We note that the calculated relativistic correction to the isotropic shielding constant is an order of magnitude smaller than the corrections to the individual tensor components.

Table 3 Relativistic corrections to the shielding tensor (in ppm)

	σ	$\Delta\sigma$	$\sigma_\perp$	$\sigma_\parallel$
RHF	26.495565[a]	1.980917	25.835260	27.816177
DHF	26.496114	1.971782	25.838853	27.810635
DHF–RHF	0.000549	−0.009135	0.003593	−0.005542

[a] For the a7Zus basis the RHF value is 26.496492 ppm

5 Rovibrational and temperature averaging

In the analysis of the shielding in homonuclear isotopomers—H_2 and D_2—we need to consider the nuclear spin statistics. For H_2, the experimental signal is due to the ortho form (o-H_2), thus only the odd J rotational states contribute. Following [6], we assume in the comparison of theory and experiment that the signal from D_2 gas can be attributed to o-D_2, and in this case only the even J states contribute.

The first set of results shown in Table 4 was obtained applying CCSD shielding and potential energy curves. The dominant effect on the shielding, due to zero-point vibrations, for H_2 is −0.35279 ppm, the temperature effects are smaller and the additional change in the shielding at 300 K is −0.01384 ppm. These values obtained with the CCSD potential are in good agreement with the results of [2], −0.355 and −0.014 ppm, respectively. The corresponding rovibrationally averaged anisotropic shieldings is $\Delta\sigma_{T=300\,K} = 1.754$ ppm.

To examine the accuracy of the results we need to consider next the adiabatic and nonadiabatic effects. We illustrate the role of the potential using the CCSD curve and two curves determined in the basis of explicitly correlated Gaussian functions (ECG). The first describes a somewhat more accurate Born–Oppenheimer potential, the second—with the energies supplemented by the adiabatic corrections—in addition differentiates the potential curves among isotopomers. The computed adiabatic corrections appear to be accurate, for instance the correction to H_2 dissociation energy, 5.773 cm^{-1}, is in very good agreement with the best recent value, 5.7711 cm^{-1} [8].

When we use the Born–Oppenheimer ECG curve (with the CCSD shielding constants) instead of the CCSD potential energy curve, we obtain slightly larger averaged shieldings, but the isotope shifts remain practically unchanged. On the other hand, adding the adiabatic corrections to the ECG curve leads to a lowering of the averaged shielding constants (by 0.00391 in H_2, 0.00295 in HD and 0.00199 ppm in D_2) and in an increase of both calculated isotope shifts by $\approx$0.00095 ppm, almost independently of the temperature. The effects are an order of magnitude larger than those caused by interchange of the CCSD and ECG potential energy curves at the Born–Oppenheimer level of theory; the adiabatic corrections to the potential are thus nonnegligible.

6 Isotope shifts

A very sensitive comparison of ab initio results and experimental data is obtained analyzing the isotope shifts and their temperature dependence. We shall discuss the results for the σ(o-D_2)–σ(HD), D shift as a function of the temperature, and for the H isotope shift σ(HD)–σ(H_2) at 300 K (this choice, following [3], reflects mainly the availability of experimental data). We do not analyze the difference σ(o-D_2)–σ(H_2), H/D, which we estimate to be ca. 0.1 ppm, since the only available experimental value—0.065(59) ppm [9]—has very large error bars.

Table 4 Temperature dependence of the shielding constants (in ppm)

T/K	H_2	HD(H)	HD(D)	D_2	HD(H)–H_2	D_2–HD(D)
CCSD potential curve (nuclear charges = 1, shielding—CCSD)						
0	26.31182	26.37810		26.43041	0.06628	0.05231
23.8	26.31182	26.37787		26.43040	0.06606	0.05253
40	26.31182	26.37627		26.43014	0.06446	0.05387
100	26.31176	26.36799		26.42102	0.05623	0.05303
150	26.31091	26.36137		26.41301	0.05047	0.05164
200	26.30818	26.35479		26.40618	0.04661	0.05139
300	26.29797	26.34164		26.39301	0.04367	0.05137
ECG potential curve (nuclear charges = 1, shielding—CCSD)						
0	26.31272	26.37901		26.43132	0.06629	0.05231
300	26.29888	26.34255		26.39393	0.04367	0.05138
ECG potential curve with adiabatic corrections (nuclear charges = 1, shielding—CCSD)						
0	26.30883	26.37606		26.42934	0.06723	0.05328
300	26.29498	26.33960		26.39194	0.04463	0.05234
ECG potential curve with adiabatic corrections, (nuclear charges = 1, shielding—MCSCF)						
0	26.31280	26.37997		26.43320	0.06717	0.05323
300	26.29896	26.34355		26.39585	0.04459	0.05230
ECG potential curve with adiabatic corrections, (modified nuclear charges, shielding—MCSCF)						
0	26.30518	26.36965	26.37883	26.42938	0.06447	0.05055
300	26.29134	26.33323	26.34242	26.39203	0.04189	0.04960

Our results are in better agreement with the ab initio values of Sundholm and Gauss than with the experiment. However, the results discussed so far have been obtained with the shielding of both nuclei equal and independent of the isotopic species. In the analysis of the corrections to the Born–Oppenheimer approximation, in addition to the changes of the potential curve also the direct effects on the shielding have to be considered. A detailed theoretical description of these effects has been recently published by Pachucki [10]. We focus below on the discussion of the isotope shifts, rather than specific shielding constants. There are two reasons for this—first, as mentioned above, for the isotope shifts there are experimental data. Secondly, the complete expressions for the corrections to the shielding constants involve nonstandard operators, leading to complicated response functions, whereas when we consider the isotope shifts (differences) most of these terms cancel out.

In the Born–Oppenheimer approximation, the electronic wave functions of all isotopomers of hydrogen molecule are the same and of $D_{\infty h}$ symmetry; therefore, at a given internuclear distance, the shielding of both nuclei is equal and the differences among isotopomers may result from the nuclear wave functions only. In order to take into account the influence of the nuclear mass on the shielding at the electronic stage of the problem, we use a modified adiabatic approximation, in which the electronic Schrödinger equation is solved with the Hamiltonian

$$\hat{H}_e = \sum_{i=1,2}\left(\frac{\hat{p}_i^2}{2} - \sum_{A=1,2}\frac{Z_A{}'}{r_{Ai}}\right) + \frac{1}{r_{12}}, \tag{2}$$

where $Z_A{}' = \mu_A Z_A$ and μ_A is the electron-nucleus reduced mass. This approach enables a description of the finite nuclear mass effect, which would otherwise require a nonadiabatic treatment. It is based on the observation that the spectrum of wave functions of hydrogen-like systems, for a fixed nucleus and with the interaction term multiplied by the reduced mass, is the same as the exact one, obtained after separation of the center of mass motion (for a discussion of the ideas underlying this approximation see [11]). Moreover, applying modified nuclear charges $Z_A{}'$ lowers the electronic wave function symmetry for mixed isotopomers like HD.

The symmetry breaking in a homonuclear, but heteroisotopic molecule is a kinetic effect. Various attempts to move respective terms of the hamiltonian to the electronic problem, usually based on a unitary transformation of the hamiltonian [12, 13], have been made in the past. Another method, in which the nuclear kinetic energy operator is partially included in the electronic hamiltonian in an approximate manner, has been proposed by Mohallem [14, 15]. The approach we use is distinct from those mentioned above, as we move a part of the potential energy operator, appearing traditionally in the electronic hamiltonian, to the nuclear hamiltonian, with the goal of making the electronic wave function resemble the nonadiabatic one [11].

We have computed the shielding constants for systems with altered nuclear charges Z_A' to estimate the first, nonadiabatic correction to the shielding constants discussed by Pachucki [10]. This correction results from the modification of the electronic wave function by the nuclear hamiltonian, which is simulated reasonably well by our method, as shown for the dipole moment of HD [11]. The corresponding results shown in Table 4 were obtained using a relatively simple (eight configurations) multiconfigurational self-consistent field (MCSCF) wave function. With unmodified nuclear charges we find the shielding constants slightly increased, but the isotope shifts differ from CCSD by less than 0.0001 ppm, hence this approximation is sufficiently accurate. In the following MCSCF calculations with modified nuclear charges, all the shielding constants are diminished: σ(H) in H_2 by 0.00762, σ(H) in HD by 0.01032, σ(D) in HD by 0.00112 and σ(D) in D_2 by 0.00382 ppm, respectively. We note that the consequences of lowering the electronic wave function symmetry in HD appear to be important. The net effects observed for $\sigma(D_2)$–σ(HD), D shift and σ(HD)–$\sigma(H_2)$, H shift, are practically the same, −0.00270 ppm. For each isotopomer the change is again almost independent of temperature.

Three more corrections to the shielding constants discussed by Pachucki [10], related to finite nuclear mass (nuclear recoil), cannot be described in this manner. We consider here only the isotope shift and note first that a significant cancellation between various terms contributing to the shielding constant occurs. When we analyze the isotope shift for a particular nucleus, we need to include only the terms which depend on the mass of the other nucleus. Moreover, we analyze here the electronic ground state of Σ symmetry, for which the nuclear and electronic contributions to the angular momentum operator differ only in sign. Thus, the corrections involving mixed electronic-nuclear response type properties, expected for nuclear-motion dependent corrections to molecular properties, can be expressed in terms of purely electronic second-order response properties. To summarize, the expressions we need for the isotope shift are significantly simpler than the general expressions given by Pachucki [10] for all the corrections to the shielding constant, which are exact to the first order in electron/nuclear mass ratio, but are also highly nontrivial to compute.

In our case, for a specified value of the internuclear distance R these three electronic contributions to the isotope shifts are therefore proportional (respectively): to $1/R$, to $\xi^p(R)/R^3$ where $\xi^p(R)$ is the paramagnetic contribution to the magnetizability, and to $\sigma^p(R)$, the paramagnetic contribution to the shielding constant. The first term for $R = 1.4\,a_0$ gives 0.00202 ppm for the correction to σ(D) in D_2 and a 0.00403 ppm correction to σ(D) in DH, so for $\sigma(D_2)$–σ(HD), D shift we get −0.00201 ppm. Similarly, we find −0.00062 ppm for σ(HD)–$\sigma(H_2)$, H shift. The last two corrections are identical for $\sigma(D_2)$–σ(HD), D shift and σ(HD)–$\sigma(H_2)$, H shift; the correction proportional to ξ^p is 0.00094 ppm and the correction proportional to σ^p is 0.00156 ppm. The changes of these corrections due to averaging at 300 K are negligible (<2%).

Table 5 Temperature dependence of the isotope shifts (in ppm)

Temperature (K)	This work[a]	Ref. [3]	Ref. [6]	Experiment[b]
σ(o-D_2)–σ(HD), D shift				
23.8	0.05253	0.0534	0.0487	0.0471 (8)
40	0.05387	0.0548	0.0496	0.0492 (3)
100	0.05303	0.0540	0.0491	0.0497 (3)
154	0.05159	0.0525	0.0482	0.0499 (10)
200	0.05139	0.0523	0.0481	0.0479 (6)
300	0.05137 (0.05015)	0.0524	0.0482[c]	0.0479 (5)[c], 0.042 (2)[d] Ref. [16]
σ(HD)–$\sigma(H_2)$, H shift				
300	0.04367 (0.04379)	0.0451		0.036 (2) Ref. [17]; 0.0359 (2)[d] Ref. [16] 0.04 (1) Ref. [18]

[a] CCSD results. For 300 K, in parentheses, values incorporating all the estimated corrections (see the text)

[b] Experimental values taken from [7], unless stated otherwise

[c] 296 K

[d] Theoretical estimates in [16] are 0.045 ppm for $\sigma(D_2)$–σ(HD), D shift and 0.038 ppm for σ(HD)–$\sigma(H_2)$, H shift

In Table 5, we compare the theoretical and experimental results for the isotope shifts (we recall that the analysis of the isotope shifts in [6] is partly based on the experimental data of [7]). For 300 K, we present in addition to CCSD results the values of both isotope shifts incorporating all the discussed above corrections. We have assumed additivity of all the effects due to the corrections to the potential curve and due to the changes in the shielding constants. Including the adiabatic and nonadiabatic effects brings the computed $\sigma(D_2)$–σ(HD), D shift closer to the experimental value, whereas the calculated σ(HD)–$\sigma(H_2)$, H shift remains too large.

7 Conclusions

An analysis of various contributions to the shielding constants indicates that to ensure higher accuracy of the results one should perform a systematic calculation going beyond the Born–Oppenheimer approximation. It appears that the errors in the shielding due to basis set incompleteness are below 0.001 ppm, the errors due to inaccuracy of the potential are similar in magnitude and we can estimate the error of rovibrationally averaged values at this level of approximation to be <0.002 ppm. The effects of adiabatic and nonadiabatic corrections to the potential and to the shielding curves are larger, even some of the estimated corrections to the isotope shifts are ≈ 0.003 ppm.

Moreover, the Born–Oppenheimer approximation does not permit the analysis of the differences between the shielding of H, D and T nuclei in mixed isotopomers of hydrogen molecule (in particular, the difference between H and D shielding in HD is required for an accurate determination od deuteron magnetic moment from NMR spectra of HD [19, 20]). Various estimates of these differences indicate that they are in the range 0.01–0.02 ppm. Our estimate of $\sigma(\mathrm{H})$–$\sigma(\mathrm{D})$ in HD, -0.009 ppm, confirms that the nonadiabatic effects should be analyzed in detail—their magnitude apparently exceeds the error bars of all the other contributions to the shielding.

We finally note that the isotropic shielding constant in H_2 serves to fix the NMR shielding scale for chemical applications of proton NMR spectroscopy. Although in these applications mainly the relative shifts are needed, the knowledge of the absolute shielding is required for instance when the nuclear magnetic dipole moments are analyzed.

The ACES II MAB [21] package has been used in the nonrelativistic CCSD calculations. In the relativistic studies, we have used the DIRAC [22] program, a version enabling the application of London atomic orbitals. The RHF and MCSCF results were obtained using the Dalton program [23].

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References

1. Sundholm D, Gauss J, Ahlrichs R (1995) Chem Phys Lett 243:264
2. Sundholm D, Gauss J, Schäfer A (1996) J Chem Phys 105:11051
3. Sundholm D, Gauss J (1997) Mol Phys 92:1007
4. London F (1937) J Phys Radium 8:397
5. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information
6. Raynes WT, Panteli N (1983) Mol Phys 48:439
7. Beckett JR, Carr HY (1981) Phys Rev A 24:144
8. Pachucki K, Komasa J (2009) J Chem Phys 130:164113
9. Wimett TF (1953) Phys Rev 91:476
10. Pachucki K (2010) Phys Rev A 81:032505
11. Strasburger K (2009) J Chem Phys 131:134103
12. Thorson WR, Choi JH, Knudson SK (1985) Phys Rev A 31:22
13. Pachucki K, Komasa J (2008) Phys Rev A 78:052503
14. Gonçalves CP, Mohallem JR (2003) Theor Chem Acc 110:367
15. Assafrão D, Mohallem JR (2007) J Phys B At Mol Opt Phys 40:F85
16. Neronov YuI, Barzakh AE, Mukhamadiev K (1975) Zh Eksp Teor Fis 69:1872
17. Evans DF (1961) Chem Indust (London), p 1960
18. Dayan E, Widenlocher G, Chaigneau M (1963) Compt Rend Acad Sci (Paris) 257:2455
19. Neronov YuI, Karshenboim SG (2003) Phys Lett A 318:126
20. Karshenboim SG, Ivanov VG, Neronov YuI, Nikolaev BP, Tolparov YuN (2005) Can J Phys 83:405
21. Aces II Mainz-Austin-Budapest-Version 2005, a quantum chemical program package, written by Stanton JF, Gauss J, Watts JD, Szalay PG, Bartlett RJ with contribution from Auer AA, Bernholdt DB, Christiansen O, Harding ME, Heckert M, Heun O, Huber C, Jonsson D, Juselius J, Lauderdale WJ, Metzroth T, Ruud K and the integral packages MOLECULE (Almlöf J and Taylor PR), Props (Taylor PR), and ABACUS (Helgaker T, Jensen HJAa, Jørgensen P, and Olsen J). See also Stanton JF, Gauss J, Watts JD, Lauderdale WJ, Bartlett RJ, Int J Quant Chem Symp 26, 879 (1992) as well as: http://www.aces2.de for the current version
22. DIRAC 04, a relativistic ab initio electronic structure program, Release DIRAC04.0 (2004), written by Jensen HJAa, Saue T, and Visscher L with contributions from Bakken V, Eliav E, Enevoldsen T, Fleig T, Fossgaard O, Helgaker T, Laerdahl J, Larsen CV, Norman P, Olsen J, Pernpointner M, Pedersen JK, Ruud K, Salek P, van Stralen JNP, Thyssen J, Visser O, and Winther T; see http://dirac.chem.sdu.dk
23. Dalton, a molecular electronic structure program, release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html