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A New Approach for Calculations of the Second-Order Magnetic Properties: Magnetic Susceptibility

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A new cost-effective approach and computational program POLMAG-3 for performing ab initio calculations of molecular magnetic susceptibility have been developed within the framework of the coupled perturbed Hartree−Fock approach based upon the simultaneous analytical dependence of both the bond order matrix and basis set functions on the corresponding perturbation parameters. The test calculations performed for a series of molecules within the proposed approach with the 6-31G basis set show good agreement with experiments.

I. Introduction

Accurate calculations of second-order molecular magnetic properties, such as magnetic susceptibility and nuclear magnetic shielding, are still challenging tasks for theoretical chemists. Presently methods for calculating these parameters are implemented at most of the standard correlated high-level quantum-chemical approaches.[1] These methods allow one to achieve chemical accuracy, but due to high CPU requirements, such calculations are still restricted only to small systems. This justifies the continuous interest in the Hartree−Fock approximation that is applicable to most medium and large systems of interest in NMR experiments, providing results of reasonable quality at reasonable computer expense.[1,2] Another problem of ab initio calculations of magnetic properties is the choice of the atomic basis set. It should be large enough to describe the effects of the applied perturbation but small enough to allow predictions of the properties for the system of interest. Usually in order to obtain reliable results it is necessary to apply extended basis sets augmented by polarization and diffuse functions.

In this paper, we propose a new cost-effective method for calculating molecular magnetic susceptibilities at the coupled perturbed Hartree−Fock (CPHF) algebraic level of theory for one-determinant wave functions. This approach takes into account the simultaneous dependence of orbital coefficients and basic functions on the perturbation parameters. Explicit analytical expressions of physically justified correction functions are generated by the solution of the nonhomogeneous Schrödinger equation for the model "one-electron atom in an external uniform field" problem, using the closed representation of Green's function. The developed method has been implemented into the standard CPHF scheme. The calculated values of magnetic susceptibility for the test series of molecules have been compared with experimental values and with the results of calculations at the conventional CPHF level.

II. Theory

The exact calculation of the physical properties of many-body systems with the quantum mechanical formalism rests first of all on the many-electron problem difficulties that can be avoided by using some approximate methods. One of the most widespread methods of the electronic wave function calculations is CPHF. Due to the approximate solution of the corresponding equations, the wave function does not provide a true description of electronic density distribution in all domains of the configuration space. However, it should be noted that even reaching the minimum value of total energy of a molecule does not ensure that reliable values of the molecular properties will be obtained, as long as they are defined by the electronic density distribution not only in the internuclear molecular space but also in peripheric regions and near-nuclei domains that virtually give no contribution to the total molecular energy value. The well-known solution to this problem is an "extension" of the initial basis set of atomic orbitals (AO) used in calculations. A traditional method for such an "extension" is the increase of the quantity of basic AOs by means of augmentation of the so-called polarization and diffuse functions to the initial set of atomic orbitals. However, in such a case, the size of the basis set obtained exceeds considerably the initial basis set size. In addition, neither the required quantity nor the functional form of the additional functions are defined by any physically justified manner. Commonly, the choice of additional basis functions depends only on the intuition and professional experience of the researcher.

In the approximation considered by us the expressions for the second-order correction $E^{(2)}$ to the energy of unperturbed molecule $E^{(0)}$ are computed as

$$E^{(2)} = 2\mathrm{Tr}[P^{(1)}W_1^{(0,0)} + P^{(0)}(W_1^{(1,0)} + W_1^{(0,1)}) + P^{(0)}W_2^{(0,0)}] \quad (1)$$

Here $W_i^{(n,m)}$ is the matrix with matrix elements $W_{ipq}^{(n,m)} = \langle \chi_p^{(n)}, \hat{W}_i \chi_q^{(m)} \rangle$; $\hat{W}_i$ corresponds to the property perturbation operator; $\chi_p^{(1)}$ is the first-order correction function to the initial basis function $\chi_p^{(0)}$.

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Needful explicit expression for the first-order density (bond order) matrix $P^{(1)}$ to the zero-order matrix $P^{(0)}$ has been derived in ref 3:

$$P^{(1)} = \sum_{a=1}^{n} \sum_{b=n+1}^{m} (C_b^{(0)} K_{ba} \tilde{C}_a^{(0)} + C_a^{(0)} \tilde{K}_{ba} \tilde{C}_b^{(0)}) - S^{-1} \mu P^{(0)} - P^{(0)} \tilde{\mu} S^{-1}, \quad (2)$$

where $K_{ba} = (\epsilon_a - \epsilon_b)^{-1}[\tilde{C}_b^{(0)}(F^{(1)} - \epsilon_a \tilde{\mu} - \epsilon_b \mu) C_a^{(0)}]$; ϵ_a are one-electron energies; $F^{(1)}$ is the first-order correction to the Fock operator matrix; μ is the matrix with elements $\mu_{pq}^{(n,m)} = \langle \chi_p^{(n)}, \chi_q^{(m)} \rangle$; S^{-1} is the matrix reverse to an overlap matrix S; and $C_a^{(0)}$ is the molecular orbital expansion coefficient.

It should be noted that eq 2 is the solution of the matrix equation

$$FP^{(1)}S - SP^{(1)}F = SPF^{(1)} - F^{(1)}PS + S^{(1)}PF - FPS^{(1)}$$

obtained by differentiating on perturbation of the Hartree−Fock−Roothaan equation for the P matrix

$$FPS = SPF$$

under the additional condition

$$P^{(1)}SP + PS^{(1)}P + PSP^{(1)} = P^{(1)}$$

which can be determined from the generalized idempotency condition

$$PSP = P$$

by being differentiated with respect to a parameter.

By multiplying the first-order equation on the left and on the right sides by the S^{-1} matrix and by inserting eq 2 with simultaneous applications of the following relations

$$S^{-1} = P + P_v, \qquad PFP = \sum_a \epsilon_a P_{aa}$$

$$PFP_v = P_v FP = 0, \qquad P_v F P_v = \sum_b \epsilon_b P_{bb}$$

where $P_v = \sum_b P_{bb}$ is a matrix which is analogous to the P matrix but constructed by using the virtual orbital coefficients C_b, one concludes the identity of both sides of the foregoing equation.

By substituting (2) into (1) one obtains

$$E^{(2)} = 2\mathrm{Tr}[\sum_{a=1}^{n} \sum_{b=n+1}^{m} (C_b^{(0)} K_{ba} \tilde{C}_a^{(0)} + C_a^{(0)} \tilde{K}_{ba} \tilde{C}_b^{(0)}) W_1^{(0,0)} + P^{(0)} W_2^{(0,0)} + P^{(0)}(W_1^{(1,0)} + W_1^{(0,1)}) - (S^{-1} \mu P^{(0)} + P^{(0)} \mu S^{-1}) W_1^{(0,0)}] \quad (3)$$

Here the first and second terms appear in the case of an unperturbed basis; the third term expresses the basis set dependence on perturbation; and the fourth term takes into account the complicated dependence of the first-order bond order matrix $P^{(1)}$ on the perturbation parameter λ [i.e., $P^{(1)} = f(\lambda, \chi(\lambda))$].

It is necessary to note that if $\chi^{(1)}$ is zero, then the expression for $P^{(1)}$ is reduced to the form arising from the standard perturbation theory that is used in almost all software packages for calculating molecular properties.

Determination of the explicit form of the first-order correction functions $\chi^{(1)}$ to the basis set AO's $\chi^{(0)}$ is based upon the solution of the inhomogeneous Schrödinger equation

$$\left[-\frac{1}{2}\Delta + V(r) - E\right]\chi(r) = \lambda \hat{W}(r) \chi(r) \quad (4)$$

where $V(r)$ is a potential that defines the form of basis set AO's and $\hat{W}(r)$ is the perturbation operator. The differential eq 4 can be reduced to the integral equation of the second kind, from the solution of which it follows that the first-order correction to the solution $\chi^{(0)}(r)$ corresponding to the homogeneous form of eq 4 ($\lambda \hat{W}(r) \equiv 0$) is determined by the relation

$$\chi^{(1)}(r) = \int G_E(\mathbf{r}, \mathbf{r}') \hat{W}(\mathbf{r}') \chi^{(0)}(\mathbf{r}') \mathrm{d}\mathbf{r}' \quad (5)$$

Here $G_E(\mathbf{r}, \mathbf{r}')$ is the Green's function of the homogeneous Schrödinger equation. For the spherically symmetrical potential $V(r)$ the Green's function can be expressed in the form

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_{l,m} g_l(r, r'; E) Y_{lm}(r_0) Y_{lm}^*(r_0') \quad (6)$$

where Y_{lm} are spherical functions of the argument $r_0 = \vec{r}/|r|$ and $g_l(r, r'; E)$ is a radial part of the Green's function $G_E(\mathbf{r}, \mathbf{r}')$.

In molecular calculations the Slater- and Gauss-type functions are the most widespread as the basis set functions

$$\chi_S(n,l,m) = N_n r^{n-1} \exp(-\xi r) Y_{lm}(r_0)$$

$$\chi_G(n,l,m) = N_n r^{n-1} \exp(-\xi r^2) Y_{lm}(r_0) \quad (7)$$

which are eigenfunctions of the homogeneous Schrödinger equations corresponding to eq 4 with the potentials

$$V_S(r) = -\frac{\xi n}{r} + \frac{A}{2r^2}$$

$$V_G(r) = 2\xi^2 r^2 + \frac{A}{2r^2} \quad (8)$$

respectively, where $A = n(n - 1) - l(l + 1)$; ξ is an orbital exponent; and N_n is a normalization factor. With this form of A the Slater- and Gauss-type functions contain the nodeless functions only, and they do not form the complete basis set because they are the solutions of the Schrödinger equation with different potentials of type (8).

In the case of dependence of the magnetic field operator $\hat{W}(r)$ on the choice of the coordinate system, the vector potential for the molecular problem is expressed as follows:

$$\hat{W}(r) = (e\hbar/2mc)\cdot[(\vec{r} - \vec{R}) \times \vec{\nabla}] = \hat{W}_0 - (e\hbar/2mc)\cdot[\vec{R} \times \vec{\nabla}]$$

where $\vec{r}$ is the electron position vector relative to a nucleus, and $\vec{R}$ is the nucleus position vector relative to the molecular reference system. Since the influence of the $\hat{W}_0$ operator on the basis function $\chi^{(0)}$ is reduced to the modification of the magnetic quantum number m, the contribution of this operator to (5) vanishes. Thus the operator $-(e\hbar/2mc)\cdot[\vec{R} \times \vec{\nabla}]$ is the appropriate perturbation operator.

The radial Green function for potentials in eq 7 can be written in a closed analytical form through the Whittaker functions.

As an example, below are represented the Slater- and Gauss-type response functions for the x-component of the perturbation operator

$$\hat{W}_x = -\frac{e\hbar}{2mc}[\vec{R} \times \vec{\nabla}]_x = \frac{e\hbar}{2mc}\left(R_z \frac{\partial}{\partial y} - R_y \frac{\partial}{\partial z}\right)$$

TABLE 1: Magnetic Susceptibilities of the Second-Row Hydrides (ppm cgs/mol)

method		HF^a	H_2O^b	NH_3^c	CH_4^d
G98/CSGT/6-31G	total	−7.88 (11)^e	−9.01 (13)^e	−10.29 (15)^e	−11.61 (17)^e
G98/CSGT/6-31G(d,p)	total	−9.12 (20)^e	−11.38 (25)^e	−13.36 (30)^e	−14.59 (35)^e
G98/CSGT/6-311++G(d,p)	total	−9.58 (29)^e	−12.29 (36)^e	−14.94 (43)^e	−16.13 (50)^e
POLMAG-3/6-31G	dia	−10.48 (11)^e	−15.06 (13)^e	−20.79 (15)^e	−28.19 (17)^e
	para	0.78 (11)^e	1.97 (13)^e	4.02 (15)^e	9.17 (17)^e
	total	−9.70 (11)^e	−13.09 (13)^e	−16.76 (15)^e	−19.02 (17)^e
expt	dia	−11.01	−14.5	−20.2	−26.682
	para	0.61	1.51	3.923	9.298
	total	−10.4	−13.12 ± 1.78	−16.3 ± 0.8	−17.4 ± 0.8

[a] Experimental values taken from ref 8. [b] Experimental values taken from ref 9. [c] Experimental values taken from ref 10. [d] Experimental values taken from ref 11. [e] Number of basis functions.

(1) Slater-type functions:

$$1s^{(1)} = \frac{N_1}{\sqrt{3}}\rho e^{-\rho}(R_z Y^S_{11} - R_y Y_{10}), \qquad \rho = \xi r$$

$$2s^{(1)} = \frac{N_2}{\sqrt{3}}\rho^2 e^{-\rho}(R_z Y^S_{11} - R_y Y_{10})$$

$$2p_x^{(1)} = 2p_x^{(0)}[\vec{R} \times \vec{r}\,]_x$$

$$2p_y^{(1)} = 2p_y^{(0)}\left\{[\vec{R} \times \vec{r}\,]_x + \frac{3}{2}R_z(1-\rho)/(\xi^2 y)\right\}$$

$$2p_z^{(1)} = 2p_z^{(0)}\left\{[\vec{R} \times \vec{r}\,]_x - \frac{3}{2}R_y(1-\rho)/(\xi^2 z)\right\}.$$

(2) Gauss-type functions:

$$s^{(1)} = -\frac{N_1}{\sqrt{3}} r e^{-\xi r2}(R_z Y^S_{11} - R_y Y_{10})$$

$$p_x^{(1)} = \frac{N_2}{\sqrt{5}} r^2 e^{-\xi r2}(R_y Y^C_{21} - R_z Y^C_{22})$$

$$p_y{}^{(1)} = N_2 r^2 e^{-\xi r2}\left[R_z\left(\frac{Y^C_{22}}{\sqrt{5}} + \frac{Y_{20}}{\sqrt{15}} - \frac{Y_{00}}{\sqrt{3}}\right) + R_y\frac{Y^S_{21}}{\sqrt{5}}\right]$$

$$p_z{}^{(1)} = N_2 r^2 e^{-\xi r2}\left[R_y\left(\frac{Y_{00}}{\sqrt{3}} + \frac{2Y_{20}}{\sqrt{15}}\right) - R_z\frac{Y^S_{21}}{\sqrt{5}}\right]$$

where Y^C_{lm} and Y^S_{lm} are the real spherical functions:

$$Y^C_{lm} = \frac{1}{\sqrt{2}}[(-1)^m Y_{lm} + Y_{l,-m}]$$

$$Y^S_{lm} = -\frac{1}{\sqrt{2}}[(-1)^m Y_{lm} - Y_{l,-m}]$$

The above-described approach leads in a natural way to the physically justified improvements of the approximate wave function in those regions of the configuration space that give the dominant contribution to the molecular properties under consideration.

It should be emphasized that the sizes of all matrixes used in the calculations coincide with those for the unperturbed zero-order basic set functions.

III. Performance of Proposed Approach

The performance of a recently developed program using the 6-31G basis set, in comparison with standard CSGT-CPHF calculations[6] with different size and quality basis sets, is illustrated by the results of the test calculations of the magnetic susceptibilities (see Tables 1 and 2 and Figure 1) for the number of species. Calculations of magnetic susceptibility for all considered molecules have been performed for the MP2/6-311G-(d) optimized geometries. Both geometry optimization and CSGT calculations have been carried out with the Gaussian 98 software.[7]

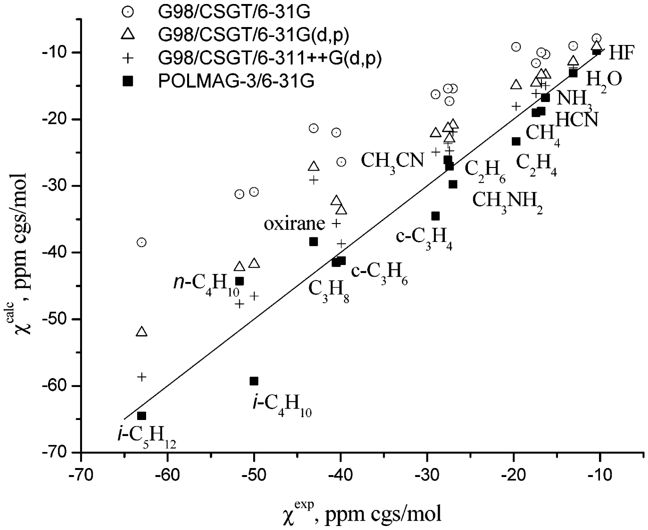

Figure 1. The calculated isotropic magnetic susceptibilities are plotted versus experimental data. The solid line has unit slope and zero intercept.

Our test sets consist of (a) ten-electron second-row hydrides HF, H_2O, NH_3, and CH_4 for which the total magnetic susceptibilities as well as the dia- and paramagnetic contributions have been measured experimentally in the gas phase (Table 1) and (b) saturated hydrocarbons up to C_5H_{12}, ethylene, cyclopropene, cyclopropane, oxirane, and nitrogen-containing molecules HCN, CH_3NH_2, and CH_3NC (Table 2).

A comparison of the calculated and experimental values clearly demonstrates the superiority of the proposed approach with the small-sized 6-31G basis set over the standard CSGT calculations with the 6-31G and 6-31G(d,p) basis sets. In most cases calculations with the new method provide even better results if compared to the CSGT calculations with the extended 6-311++G(d,p) basis set. Linear regression analyses show that the results calculated at the POLMAG-3/6-31G level have the slope closest to unity and the smallest intercept. It should be noted that the 6-311++G(d,p) basis set is about three times larger than the 6-31G basis set so it requires more than 100 times more CPU time for performing analogous calculations.

The discrepancies which one can see in Table 2 for i-C_4H_{10} between the experimental data and the current results indicate

TABLE 2: Magnetic Susceptibilities of the Series of Molecules (ppm cgs/mol) and Parameters of the Linear Regression Equation $\delta_{\mathrm{expt}} = a\delta_{\mathrm{calc}} + b$[a]

molecule	G98/CSGT/ 6-31G	G98/CSGT/ 6-31G(d,p)	G98/CSGT/ 6-311++G(d,p)	POLMAG-3/ 6-31G	expt
C_2H_6	−17.29	−22.93	−24.72	−27.06	−27.40[b] (−26.8)[c]
C_3H_8	−22.00	−32.33	−35.62	−41.48	−40.5[d] (−38.6)[c]
n-C_4H_{10}	−30.89	−41.77	−46.51	−59.3	−50.0[e]
i-C_4H_{10}	−31.25	−42.25	−47.69	−44.27	−51.7[e] (liquid)
i-C_5H_{12}	−38.47	−52.01	−58.66	−64.49	−63.0 to −64.0[e]
C_2H_4	−9.14	−14.95	−18.04	−23.31	−19.70[b] (−18.8)[c]
c−C_3H_6	−26.42	−33.73	−38.67	−41.24	−39.9[d] (−39.2)[c]
c−C_3H_4	−16.27	−22.17	−24.92	−34.53	−29.0[f]
oxirane	−21.35	−27.22	−29.08	−38.36	−43.1[d] (liquid)
HCN	−9.99	−13.34	−14.67	−18.81	−16.8[f]
CH_3NH_2	−15.42	−20.89	−21.90	−29.78	−27.0[g]
CH_3NC	−15.39	−21.38	−23.66	−26.10	−27.6[h]
R	0.98	0.99	0.98	0.97	
A	1.64	1.21	1.07	0.96	
B	−0.75	−0.93	−1.68	−0.42	

[a] Linear regression equation includes data for all of calculated compounds from Tables 1 and 2. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Reference 15. [f] Reference 8. [g] Reference 16. [h] Reference 17.

that there is a strong influence of intramolecular forces on the susceptibilities. Such discrepancies are noted for the systems for which experimental liquid-phase values are used for comparison.

IV. Conclusions

We have shown that the proposed approach for calculating molecular magnetic susceptibility, based upon the simultaneous analytical dependence of both the density (bond order) matrix and basis set functions on the corresponding perturbation parameters within the framework of the coupled Hartree−Fock theory, is very promising for chemical applications. The POLMAG-3 program can be used for fast and accurate predictions of the magnetic susceptibility of large molecules with use of small size basis sets. It is a cost-effective alternative to the time-consuming calculations at the standard (CPHF) level that requires the application of very large basis sets.

The POLMAG-3 program is under further development. Forthcoming applications include ab initio calculations of nuclear magnetic shielding.

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References and Notes

(1) Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, *99*, 293.

(2) Rossikhin, V. V.; Okovytyy, S. I.; Kasyan, L. I.; Voronkov, E. O.; Umrikhina, L. K.; Leszczynski J. *J. Phys. Chem. A* **2002**, *106*, 4176.

(3) Rossikhin, V. V.; Morozov, V. P. *Teor. Eksp. Chim.* **1966**, *2* (No. 4), 528.

(4) Rossikhin, V. V.; Kuz'menko, V. V.; Voronkov, E. O. *J. Phys. Chem.* **1996**, *100*, 19801.

(5) Hostler, L. *J. Math. Phys*. **1964**, *5*, 591.

(6) Keith, T. A.; Bader, R. H. W. *Chem. Phys. Lett*. **1992**, *194*, 1.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *7*, 23.

(9) Thomsen, K.; Swanstrom, P. *Mol. Phys.* **1973**, *26*, 735.

(10) Arrighini, G. P.; Maestro, M.; Moccia, R. *J. Chem. Phys.* **1968**, *49,* 882.

(11) Arrighini, G. P.; Maestro, M.; Moccia, R. *J. Chem. Phys.* **1968,** *49*, 2224.

(12) Oldenziel, J. G.; Trappeniers, N. J. *Physica A* **1976**, *82A*, *565*, 581.

(13) Barter, C.; Meisenheimer R. G.; Stevenson, D. P. *J. Chem. Phys.* **1960**, *64*, 1312.

(14) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press, New York, 1967; Vol. 1,

(15) Hellwege, K. H.; Hellwege A. M. *Landolt-Börnstein, Zahlenwerte und Funktionen, H. 10*; Springer: New York, 1967.

(16) Mulay, L. N.; Bordeaux, E. A. *Theory and Application of Molecular Diamagnetism*; Wiley: New York, 1976.

(17) Hellwege, K. H.; Hellwege A. M. *Landolt-Börnstein, Zahlenwerte und Funktionen, New Series H*; Springer: New York, 1987; Vol. 6, p 14.