Ab Initio Quantum Chemical Calculation as a Tool of Evaluating Diamagnetic Susceptibility of Magnetically Levitating Substances

Y Fujiwara¹ and Y Tanimoto²

¹ Department of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

² Faculty of Pharmacy, Osaka Ohtani University, Nishikiorikita, Tondabayashi 584-8540, Japan

E-mail: fuji0710@sci.hiroshima-u.ac.jp

Abstract. On magnetic force evaluation necessary for magnetically levitated diamagnetic substances, isotropic diamagnetic susceptibility estimation by the ab initio quantum chemical calculation using Gaussian03W was verified for more than 300 molecules in a viewpoint of the accuracy in the absolute value and the calculation level affording good cost performance. From comparison, the method of B3PW91 / 6-311+G(d,p) was found to give the adequate absolute value by the relation of (observed) = (1.03 ± 0.005) x (calculated) - (1.22 ± 0.60) x 10⁻⁶ in a unit of cm³ mol⁻¹ and good cost performance.

1. Introduction
Owing to recently readily available superconducting magnets possessing a strong magnetic field gradient, many studies have been carried out for diamagnetic substances in a magnetic levitation environment, which is created by magnetically simulated microgravity resulting from a balance between gravitational and upward diamagnetic forces simultaneously working on the substances [1-4]. The diamagnetic force is evaluated by a product of the isotropic magnetic susceptibility of diamagnetic substances, the applied magnetic field intensity, and the magnetic field gradient. However, in some cases of photo-generated labile molecular reaction intermediates and/or molecular assemblies such as J-aggregates in equilibrium with the component molecules, in general it is not easy to directly measure the susceptibility by means of SQUID (Superconducting Quantum Interference Device) due

Scheme 1. A photochemical reaction scheme yielding a colored solution upon photo-irradiation (hv).

© 2009 IOP Publishing Ltd
to the instability of intermediates and/or the mixture of substances.

Recently, Tanimoto’s group elucidated intriguing effects of the magnetically simulated microgravity and hypergravity on a movement behavior of photo-chemically colored solution surrounded by an un-reacted, colorless solution inside a cuvette [5, 6]. The scheme1 illustrates one of the photoreactions upon irradiation [5].

The behavior dependent on the microgravity and hypergravity was considered by magnetic and gravitational forces operating on each diamagnetic substance (CMTE and PI as solutes and benzene as a solvent) lying before and after photo-irradiation, respectively. However, the PI solute in benzene was too unstable against the light to isolate purely and keep it stably while the susceptibility measurement with SQUID. Thus, the isotropic diamagnetic susceptibility estimation using the ab initio quantum chemical calculation was performed by a combination of a method B3LYP based on the density functional theory (DFT) and a basis set 6-31G, which was considered to be a proper calculation level in those days. However, it was not in advance confirmed whether the calculation procedure gives exact absolute values. In the other report, further, the experimental observation of efficient magnetic orientation of molecular assemblies, porphyrin-derived nanorods, caused by hypergravity was also interpreted by an imbalance in the magnetic and gravitational forces working on the diamagnetic nanorods and surrounding solvent. Yet, the accurate susceptibility estimation of the nanorod still remains difficult due to equilibrium of the rod with the precursor, porphyrin [7].

In such cases, a theoretical calculation method giving exact absolute values of the susceptibility would wield its power. Although some successful semi-empirical calculation methods such as a Pascal’s method are reported so far for the purpose [8], unfortunately there seems to be no semi-empirical method which does not only afford the accurate absolute value of susceptibility but also is available throughout various chemical compounds regardless of the component chemical element. In other words, taking account of the current situation of many kinds of diamagnetic substances applied to the magnetic levitation environment, one useful theoretical calculation method capable of treating such diamagnetic molecular compounds simultaneously and consistently is indispensable.

By the way, an ab initio quantum chemical calculation program such as Gaussian is well-known to treat a wide variety of chemical elements. And, there were studies treating the susceptibility calculation for as small size of molecules as benzene by the ab initio calculation [9-12]. However, the size of target molecular compounds which we hope to know the susceptibility is much larger than benzene, as PI shown in scheme 1. In this work, therefore, the commercially purchasable ab initio program Gaussian was verified both about whether it can give the accurate absolute values of isotropic diamagnetic susceptibility in as many large compounds composed of various chemical elements as possible and about the calculation level affording good cost performance. Additionally speaking of an important reason for the verification, this calculation method provides the anisotropic terms of susceptibility at the same time [11, 12], being greatly helpful when the magnetic orientation based on the susceptibility anisotropy is associated with the magnetic force as observed in the above-mentioned nanorods under the hypergravity environment [7], though it is not referred in this study.

2. Calculation

In the isotropic diamagnetic susceptibility estimation by the ab initio quantum chemical calculation, the accuracy in absolute values and wide availability for many large molecular compounds were verified by means of a commercially purchasable calculation program of Gaussian03W (Gaussian, Inc.) for a Windows operating system. Two revisions of B.04 and E.01 of the program were used properly for a single central processing unit (CPU) and for multi-CPUs, respectively, according to hardware of an operated computer (1 - 8 pieces of Intel Xeon CPUs operated at one frequency in a range of 2.4 - 3.6 GHz). As a target of comparison in the calculation, more than 300 diamagnetic molecular compounds were chosen, whose experimental susceptibilities were already measured with instruments such as SQUID. Typical compounds whose susceptibilities are listed in the familiar literature often referred [13, 14] were mainly taken in this study.
Prior to the susceptibility estimation in each target molecular compound, the structural optimization was carried out by a frequently used combination of a B3LYP method [15, 16] based on the density functional theory (DFT) [17] and a 6-31+G(d) basis set [18], abbreviated to B3LYP / 6-31+G(d) hereafter. Subsequently, the susceptibility estimation with a IGAIM method [11] was attempted in respective combinations of the “method / basis set” of B3LYP / 6-31G, B3PW91 / 6-311+G(d), and B3PW91 / 6-311+G(d,p) [15, 19, 20], where a B3PW91 method is superior to B3LYP in the calculation accuracy. The superiority comes from a difference in the DFT procedures. The general sense on the order of superiority in the basis sets is 6-311+G(d,p), 6-311+G(d), 6-31+G(d), and 6-31G. The superiority of the first basis set to the second one arises from the enhanced contribution of a hydrogen atom. The superiority of the second one to the third one is based on the number of orbital functions utilized, and that of the third one to the last one depends on addition of diffused orbital function and the enhanced contribution of heavy atoms besides a hydrogen atom.

3. Results and Discussion

In use of this kind of theoretically calculated values in place of actually observed ones, how exactly the calculation procedure reproduces the observed values is a key point. Actually, however, the degree of reproduction greatly changes depending on the calculation procedure. In such a case, therefore, it is a general way to discuss the calculation precision by comparing many compounds in order to dig out the adequate calculation procedure. Further, it is a usual manner to induce a relationship applied to the calculated and observed values from the discussion and make a deduction about an individual value by means of its relationship. In fact, calculations for g values of paramagnetic species and infrared frequencies of organic compounds were carried out by this manner [21, 22]. Thus, we obey the same manner in this work and introduce an example of photochemistry shown in scheme 1 to which was applied the relationship between the calculated and observed isotropic diamagnetic susceptibility values and thereby which was discussed more quantitatively.

3.1. Calculation of Isotropic Diamagnetic Susceptibility Values

In the first place, we checked how exactly the calculation procedure of B3LYP / 6-31G, which was used in the study by Tanimoto’s group [5], estimates an experimentally observed susceptibility value. However, its procedure never reproduced the experimental value even for a typical compound of benzene. The calculated value (-35.6 x 10^-6 cm^3 mol^-1) did not reach even 70 % of the experimental one (-54.8 x 10^-6 cm^3 mol^-1) [13, 14]. Therefore, we initiated to upgrade the calculation procedure and seek its reproducibility of the value according to a usual manner described above.

As mentioned above, the more than 300 target diamagnetic molecular compounds used for the isotropic diamagnetic susceptibility estimation by Gaussian03W were selected carefully so as to prove the accuracy and wide availability of the calculation method and thereby the validity of use, as follows. Their constituent chemical elements widely spread up to bromine in the periodic table, and cover usual inorganic and organic compounds. And, neutral, mono-ionic, or zwitterionic charge types of compounds are included when necessary. The compounds are also adopted, which possess aromatic groups like a benzene ring and/or the larger and more complex unsaturated chemical bonds. The compounds having a diamagnetic metal ion inside the molecular framework are included as well, and thus the largest molecular weight ranges to more than 500. As one more important viewpoint, a range of the diamagnetic susceptibility to be verified is taken into account so as to be beyond - 400 x 10^-6 cm^3 mol^-1, where most of general diamagnetic compounds seem to be distributed.

Figure 1 shows results of the susceptibility calculation by a B3PW91 / 6-311+G(d) method of Gaussian03W. In two graphs on figure 1, calculated values in a horizontal axis are plotted against experimentally observed ones in a vertical axis. An area in the susceptibility range form 0 to 150 x 10^-6 cm^3 mol^-1 is extended in the right-hand side of figure 1 in addition to a graph depicting the overall data in the left-hand side. Approximately 270 data appear in the extended graph. The good linear relationship appears between the calculated and observed susceptibilities. As a result of the linear
least-squares method toward all of the data, the following fitted equation was obtained, which accordingly seems also available to estimate the susceptibility unknown due to no measurement.

\[
\text{(observed or unknown)} = (1.06 \pm 0.009) \times \text{(calculated)} - (3.17 \pm 0.87) \times 10^{-6} \quad \text{in a unit of cm}^3 \text{ mol}^{-1} \quad (1)
\]

with a correlation coefficient (0.989), indicating a good linear relationship. The two facts of the slope (1.06) very close to a unity and the negligibly small intercept (-3.17 x 10^{-6}) point out validity of this calculation method as a tool of directly giving fairly accurate absolute values of the susceptibility. In fact, the straight lines calculated by (1) are well superimposed on the plots in figure 1.

Next, let us see figure 2 showing the same kind of graphs in the case of a B3PW91 / 6-311+G(d,p) method where the contribution of hydrogen atoms carries weight compared with the above-mentioned case of B3PW91 / 6-311+G(d). There exists a better linear relation between the calculated and observed susceptibilities as expressed by the following fitted equation.

\[
\text{(observed or unknown)} = (1.03 \pm 0.005) \times \text{(calculated)} - (1.22 \pm 0.60) \times 10^{-6} \quad \text{in a unit of cm}^3 \text{ mol}^{-1} \quad (2)
\]

with a better correlation coefficient (0.996). Detectable effects of a 6-311+G(d,p) basis set superior to 6-311+G(d) are seen in (2). The slope (1.03) further approached a unity. The intercept (-1.22 x 10^{-6}) diminished toward zero more and more. Moreover, standard deviations in both values decreased. This

**Figure 1.** Plots of isotropic diamagnetic susceptibilities calculated by B3PW91 / 6-311+G(d) against observed ones.

**Figure 2.** Plots of isotropic diamagnetic susceptibilities calculated by B3PW91 / 6-311+G(d,p) against observed ones.
effect was represented in figure 2 as a smaller extent of deviation of plots from the straight line simulated by (2) in comparison with figure 1. Figure 3 evaluates the degree of deviation with a percentage of $100 \times (\text{observed} - \text{calculated}) / \text{observed}$. Although there are a few plots in the noticeable divergence around $-20 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ near zero, most (about 80 %) of plots are kept inside the value of 10 %. These results are interpreted conclusively as a result of the better basis set employed. As an inevitable consequence, therefore, (2) is a better relation formula available for the isotropic diamagnetic susceptibility estimation. The parameters so far obtained are summarized in table 1 again.

**Table 1.** Parameters $\alpha$ and $\beta$ obtained by the ab initio calculation in this study, which are available for the estimation of isotropic diamagnetic susceptibility (cm$^3$ mol$^{-1}$) not obtained.

| DFT method / basis set | Parameter $\alpha^a$ | Parameter $\beta^a$ (cm$^3$ mol$^{-1}$) |
|------------------------|----------------------|----------------------------------------|
| B3PW91 / 6-311+G(d)    | $1.06 \pm 0.009$     | $-(3.17 \pm 0.87) \times 10^{-6}$     |
| B3PW91 / 6-311+G(d,p)  | $1.03 \pm 0.005$     | $-(1.22 \pm 0.60) \times 10^{-6}$     |

$^a$ Used in an equation of $(\text{observed or unknown value}) = \alpha \times (\text{calculated value}) + \beta$.

In the calculation here, all of the target compounds were respectively treated as those in a vacuum, meaning that they are respectively an isolated compound lacking interactions with other substrates such as themselves or solvents. As depicted in figures 1 and 2, however, the calculated values were straightforwardly compared with the observed ones which were practically measured in chemical media. This indicates that the relationships of (1) and (2) include contribution of various interactions of many compounds with the media comprehensively. Therefore, the scattering in figure 3 might partly result from such a treatment. The relatively large deviation in a small size of compounds might arise due to the same reason if they specifically tend to be affected by the surrounding conditions. Thus, the calculation should be carried out originally by the procedure capable of expressing such interactions individually. For instance, in the case of a solution phase where a reaction in scheme 1 occurs, influence of a solute - liquid solvent interaction should be taken into account. However, since no meaningful difference was detected between preliminary model calculations without and with the influence of a solvent, a direct use of the relationship of (2) was considered to be the best way at the present stage to estimate the magnetic force.
3.2. Application of the Calculated Susceptibility Values to the Photo-Generated Labile Reaction Intermediate

As described in the section of introduction, Tanimoto’s group had already employed the ab initio calculation for the isotropic diamagnetic susceptibility estimation of solutes CMTE and PI to explain the movement of a photo-chemically colored solution [5]. The fundamental combination of B3LYP / 6-31G used was considered to be a proper calculation level in those days. The calculated susceptibilities and resulting forces are summarized in Table 2 together with the results by (2) of this study.

Table 2. Isotropic diamagnetic susceptibilities of CMTE and PI obtained by the ab initio calculation, differences in their diamagnetic forces under each of the microgravity (-1300 T^2 m^(-1)) and hypergravity (1000 T^2 m^(-1)), and their total forces expressed with a volume V of the PI solution.

| Study                        | Isotropic diamagnetic susceptibility (10^{-6} cm^3 mol^{-1}) | Difference in diamagnetic forces between CMTE and PI (10^{-5} N) | Total force (N) |
|------------------------------|-------------------------------------------------------------|------------------------------------------------------------------|-----------------|
|                              | CMTE (colorless)                                            | PI (colored)                                                    | Microgravity   |
| The study of Tanimoto’s group | -149.3481                                                   | -149.3517                                                       | 7.0 V          |
| This study by (2)             | -195.3434                                                   | -180.3303                                                       | -29000 V       |
|                              |                                                             |                                                                  | 23000 V        |

a) Taken from [5].

In the study of Tanimoto’s group, the total force operating on the colored solution generated upon photo-irradiation was explained by the following equation.

\[
\text{(total force)} = \text{(buoyancy based on the density change of solution as a difference in gravitational forces)} + \text{(magnetic force on the solvent benzene based on the susceptibility change by Joule heating)} + \text{(magnetic force based on the CMTE and PI susceptibilities)}
\]

And, it was found that a difference (0.0036 x 10^6 cm^3 mol^{-1}) in the calculated susceptibilities (-149.3481 x 10^6 and -149.3517 x 10^6 cm^3 mol^{-1}) of the two solutes was too tiny to recognize a meaningful difference in their diamagnetic forces (7.0 V x 10^5 and 5.4 V x 10^5 N) of the microgravity and hypergravity environments, indicating no significant responsibility of their magnetic forces on the movement of colored solution. Although the large difference in diamagnetic forces means large contribution to the total force, the value in an order of 10^5 N is anyway too small. Actually, the total forces (0.41 V and 10.09 V N) on the colored solution were successfully explained by the buoyancy and the magnetic force on solvent benzene originated in the susceptibility change by Joule heating upon photo-irradiation.

By contrast, it was found that the susceptibilities (-195.3434 x 10^6 and -180.3303 x 10^6 cm^3 mol^{-1}) of the two solutes calculated in this study were apparently different from each other and the order was reversed. As a result of these new susceptibilities whose gap became larger, the difference in diamagnetic forces on CMTE and PI also became large under the microgravity (from 7.0 V x 10^5 to -29000 V x 10^5 N) and hypergravity (from -5.4 V x 10^5 to 23000 V x 10^5 N) environments, respectively. The difference between their values (-29000 V x 10^5 and 23000 V x 10^5 N) thereby widened greatly. Nevertheless, these changes resulted in having little influence on the total forces (0.12 V and 10.32 V N) compared with those (0.41 V and 10.09 V N) of Tanimoto’s group. Thus, according to the reliable susceptibilities calculated by the relationship of (2) whose validity of use was
verified in this study, it was reconfirmed that the total force was limited by the buoyancy and the magnetic force on the solvent rather than the magnetic forces on the two solutes, as suggested by Tanimoto’s group. Therefore, the ab initio calculation with B3PW91 / 6-311+G(d,p) giving the accurate absolute value of susceptibility enabled quantitative and thereby fruitful discussion based on the refined data.

4. Conclusion

On the magnetic force evaluation necessary for magnetically levitated diamagnetic substances, the ab initio quantum chemical calculation using Gaussian03W was verified in a viewpoint of the accuracy of isotropic diamagnetic susceptibility for large size of molecular compounds composed of chemical elements up to bromine in the periodic table. From comparison of the two methods of B3PW91 / 6-311+G(d) and B3PW91 / 6-311+G(d,p), the latter was found to give the considerably accurate absolute value by the relation of (observed) = (1.03 ± 0.005) x (calculated) - (1.22 ± 0.60) x 10^{-6} in a unit of cm³ mol⁻¹. From the proportional coefficient greatly close to a unity and negligible offset in the equation, it is not too much to say that this method directly calculates a real value unnecessary to correct. Therefore, this method is also suitable for the unknown susceptibility estimation. Although, of course, we confirmed that some of other “method / basis set” calculations more complex and more sophisticated than it afforded better results in which the deviation became narrower, the method of B3PW91 / 6-311+G(d,p) used in this study was found to be stressless and give good cost performance in both a CPU time and a price of a personal computer needed for calculation. Each of almost calculations carried out in this study was enough fast to finish in several days at most.

Acknowledgment

This work was partly supported by Grants-in-Aid for Scientific Research of Area 767 No. 15085208 (Priority Area “Innovative utilization of strong magnetic fields”) from MEXT of Japan and by JSPS Asian Core Program “Construction of the World Center on Electromagnetic Processing of Materials”.

References

[1] Beaugnon E and Tournier R 1991 Nature 349 470
[2] Berry M V and Geim A K 1997 Eur. J. Phys. 18 307
[3] Ikezoe Y, Hirota N, Nakagawa J and Kitazawa K 1998 Nature 393 748
[4] Mogi I, Takahashi K and Hirota N 2006 Springer Series in MATERIALS SCIENCE 89, Magneto-Science, Magnetic Field Effects on Materials: Fundamentals and Applications, ed M Yamaguchi and Y Tanimoto (Japan: Kodansha and Berlin: Springer-Verlag) pp 41-70
[5] Duan W, Fujiwara M and Tanimoto Y 2004 Jpn. J. Appl. Phys. 43 8213
[6] Koyama F and Tanimoto Y 2006 Mol. Phys. 104 1703
[7] Fujiwara Y, Shibata N, Matsumoto Y and Tanimoto Y 2007 J. Magn. Magn. Mater. 310, 2859
[8] Pasacal P 1908 Compt. Rend. 147 56
[9] Van Vleck J H 1932 The Theory of Electric and Magnetic Susceptibilities (Oxford: Univ. Press)
[10] Bhargava S and Ray N K 1979 Indian J. Chem. 18A 508
[11] Keith T A and Bader R F W 1992 Chem. Phys. Lett. 194 1
[12] Ruud K, Helgaker T, Bak K L, Jörgensen P and Jensen H J A 1993 J. Chem. Phys. 99 3847
[13] Gupta R R 1986 LANDÖLT-BORNSTEIN Numerical Data and Functional Relationships in Science and Technology New Series vol 16, ed Hellwege K -H and Hellwege A M (Berlin: Springer-Verlag)
[14] 2008 CRC Handbook of Chemistry and Physics, ed Lide D R (Boca Raton, FL: CRC Press / Taylor and Francis)
[15] Becke A D 1993 J. Chem. Phys. 98 5648
[16] Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785
[17] Hehnenberg P and Kohn W 1964 Phys. Rev. 136 B864
[18] Ditchfield R, Hehre W J and Pople J A 1971 J. Chem. Phys. 54 724
[19] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 Phys. Rev. B 46 6671
[20] McLean A D and Chandler G. S. 1980 J. Chem. Phys. 72, 5639
[21] Neese F 2001 J. Chem. Phys. 115 11080.
[22] Yoshida H, Takeda K, Okamura J, Ehara A and Matsuura H 2002 J. Phys. Chem. A 106 3580.