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Density functional theory calculation of 2p core-electron binding energies of Si, P, S, Cl, and Ar in gas-phase molecules

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Received 24 March 2005; received in revised form 30 August 2005; accepted 11 September 2005

Available online 28 October 2005

Abstract

Density functional theory (DFT) calculations have been performed on the gas-phase 2p core-electron binding energies (CEBEs) of Si, P, S, Cl, and Ar in 145 cases using the following procedure: ΔE_{KS} (scalar-ZORA + E_{xc})/TZP//HF/6-31G(d). ΔE_{KS} is the difference in the total Kohn–Sham energies of the 2p-ionized cation and the neutral parent molecule calculated by DFT using different exchange-correlation functionals E_{xc} with triple-zeta polarized basis set, at molecular geometry optimized by HF/6-31G(d), and relativistic effects have been estimated by scalar zeroth-order regular approximation. Among the 26 functionals tested, the form of E_{xc} giving the best overall performance was found to be the combination of OPTX exchange and LYP correlation functionals. For that functional, the average absolute deviation (AAD) of the 145 calculated CEBEs from experiment is 0.26 eV. There are seven other exchange-correlation functionals that led to AADs of less than 0.30 eV. Some functionals give lower AADs than E_{xc} = OPTX-LYP for some individual elements. In the case of Si, for example, the combination of either mPW91-PBE or Becke88-Perdew86 led to an AAD of only 0.10 eV for 56 silicon-containing molecules. Another example is the case of the argon atom, for which the choice of E_{xc} = OPTX-Perdew86 yields a value for CEBE equal to the experimental value.

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Keywords: ESCA; XPS; Si(2p); P(2p); S(2p); Cl(2p); Ar(2p); L-shell ionization

1. Introduction

The use of density functional theory (DFT) in atomic, molecular, and condensed-phase calculations keeps increasing every year, reaching the level of 50%, if not more, of all quantum chemical calculations reported in the literature. When one uses DFT for molecular calculations, the choice of functionals is of fundamental importance. So far, there is no single functional which is perfect for accurate prediction of every kind of physical and chemical properties. Therefore, it is important to know which is the best functional for the molecular properties that one is investigating. Many functionals have been proposed and some of them are successful for calculating certain type of molecular properties.

For the calculation of 1s core-electron binding energies (CEBEs) of C to F atoms in molecules, we have previously reported the results of our investigation in testing many functionals and basis sets [1]. The efficient method we found may be abbreviated as:

$$\Delta E_{\text{KS}} (\text{PW86x-PW91c})/\text{TZP} + C_{\text{rel}}//\text{HF}/6-31\text{G(d)},$$

with an average absolute deviation (AAD) of 0.16 eV from experiment. The functional combination is the Perdew–Wang 1986 exchange (PW86x) functional [2] and the Perdew–Wang 1991 correlation (PW91c) functional [3]. TZP stands for triple-zeta polarized basis set of Slater-type orbitals (STOs) available in the Amsterdam Density Functional (ADF) program package [4]. C_{rel} is a small empirical relativistic correction [5]. All the calculations were performed on the molecules at the geometry optimized by standard Hartree–Fock (HF) method using polarized split valence basis set of contracted Gaussian-type orbitals (CGTOs).

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Is the best method of calculating 1s CEBEs of C to F in molecules also the best for calculating 2p CEBEs of Si, P, S, Cl, and Ar? The purpose of the present work is to search for the best procedure of calculating 2p CEBEs of Si, P, S, Cl, and Ar in gas-phase molecules.

After some preliminary studies, we decided to reduce the small complication of the effect of spin-orbital interactions and calculate the weighted average of the 2p CEBEs, called CEBE($\langle 2p \rangle$), or simply $\langle 2p \rangle$, in this paper and defined as:

$$\langle 2p \rangle = \frac{2\text{CEBE}(2p_{3/2}) + \text{CEBE}(2p_{1/2})}{3} \quad (1)$$

For some molecules, experimental values corresponding to $\langle 2p \rangle$ are available; for some other molecules, both CEBE($2p_{3/2}$) and CEBE($2p_{1/2}$) have been reported and we use Eq. (1) to evaluate $\langle 2p \rangle$. For many P- and S-containing molecules, however, experimental values are available only for CEBE($2p_{3/2}$). In such a case, experimental $2p_{3/2}$ CEBE values found in the literature have been converted to $\langle 2p \rangle$ with Eq. (2) in order to compare theory with experiment.

$$\langle 2p \rangle = \text{CEBE}(2p_{3/2}) + \frac{\Delta 2p}{3} \quad (2)$$

where $\Delta 2p$ is the splitting between $2p_{1/2}$ and $2p_{3/2}$ levels defined in Eq. (3):

$$\Delta 2p = \text{CEBE}(2p_{1/2}) - \text{CEBE}(2p_{3/2}) \quad (3)$$

Table 1 lists experimental CEBE($2p_{1/2}$) and CEBE($2p_{3/2}$) as well as $\Delta 2p$ values calculated with Eq. (3). The $\Delta 2p$ values corresponding to each of the third-row elements remain fairly constant and the average value is used in Eq. (2) when experimental values for CEBE($2p_{1/2}$) are not available.

2. Method of calculation

In this work, the ADF program [4] was employed to calculate 2p CEBEs of Si, P, S, Cl, and Ar in gas-phase molecules, using the method:

$$\Delta E_{KS} (\text{scalar} - \text{ZORA} + E_{xc}) / \text{TZP} / \text{HF}/6-31\text{G(d)}.$$

In this procedure, relativistic effects were estimated by scalar zeroth-order regular approximation (ZORA) [22–24] and the total Kohn–Sham energies were calculated with a TZP basis set [4] at the geometry optimized in a standard HF/6–31G(d) step. E_{xc} is exchange-correlation functional used in the DFT calculation. We followed the previous work [1] in computing vertical CEBEs. In other words, all calculations were carried out only at the optimized geometry of the neutral parent molecule. Finally, in the specification of the occupation numbers of the Kohn–Sham MOs in a molecule, the core hole is smeared over the three 2p orbitals of the elements Si to Ar. Instead of E_{xc} , the exchange-correlation potential V_{xc} known as statistical average of orbital potentials (SAOP) [25] was tested in our earlier study of 1s CEBEs of C to F [1]. The density obtained with $V_{xc} = \text{SAOP}$ was used to calculate the energy using various E_{xc} functionals. It was found that such a procedure improved the performance of

Table 1
Experimental CEBE($2p_{1/2}$) and CEBE($2p_{3/2}$) values

Molecules	CEBE			$\Delta 2p$ split	References
	$2p_{1/2}$	$2p_{3/2}$	$\langle 2p \rangle$		
SiH ₄	107.8	107.2	107.40	0.65	[6]
SiF ₄				0.60	[7]
SiF ₄	111.4	110.8	111.00	0.55	[6]
SiF ₄	112.45	111.84	112.04	0.61	[8]
SiCl ₄	110.76	110.24	110.41	0.52	[8]
SiBr ₄	110.32	109.72	109.92	0.60	[8]
Silica				0.598	[9]
Average for Si				0.60	
P “molecule”	137.2	136.2	136.5	1.00	[10]
PH ₃	138.2	137.3	137.6	0.95	[6]
PF ₃	141.97	141.04	141.35	0.93	[11]
Average for P				0.96	
CS ₂	171.0	169.8	170.20	1.2	[12]
OCS	171.8	170.6	171.00	1.2	[12]
SF ₆	181.5	180.2	180.63	1.3	[13]
SF ₆	181.7	180.4	180.83	1.3	[14]
H ₂ S	172.2	171.1	171.47	1.1	[6]
H ₂ S	171.5	170.2	170.63	1.3	[14]
S ₈				1.2	[15]
Average for S				1.22	
HCl	208.7	207.1	207.63	1.65	[6]
HCl	209.01	207.38	207.92	1.63	[16]
MeCl	207.90	206.26	206.81	1.64	[16]
EtCl	207.56	205.92	206.47	1.64	[16]
Pr ⁿ Cl	207.45	205.81	206.36	1.64	[16]
Pr ⁱ Cl	207.25	205.62	206.16	1.63	[16]
Bu ^t Cl	207.00	205.38	205.92	1.62	[16]
CH ₂ Cl ₂	208.25	206.62	207.16	1.63	[16]
CHCl ₃	208.50	206.86	207.41	1.64	[16]
CCl ₄	208.73	207.04	207.60	1.69	[16]
FCCl ₃	208.81	207.20	207.74	1.61	[16]
F ₂ CCl ₂	209.10	207.47	208.01	1.63	[16]
F ₃ CCl	209.44	207.83	208.37	1.61	[16]
Cl ₂	209.45	207.82	208.36	1.63	[16]
ClF	210.83	209.18	209.73	1.65	[16]
BCl ₃	208.6	207.0	207.53	1.6	[17]
CIBEt ₂	207.4	205.8	206.33	1.6	[17]
SiCl ₄	208.23	206.61	207.15	1.62	[8]
Average for Cl				1.63	
Ar	250.7	248.6	249.3	2.1	[18]
Ar	250.55	248.52	249.20	2.03	[19]
Ar	250.78	248.63	249.35	2.15	[13]
Ar	250.7	248.6	249.3	2.07	[20]
Ar	250.78	248.63	249.35	2.15	[21]
Ar	250.56	248.45	249.15	2.11	[14]
Ar	250.53	248.39	249.10	2.14	[14]
Average for Ar			249.25	2.11	

$\langle 2p \rangle$ is the weighted average. $\Delta 2p$ is the split between $2p_{3/2}$ and $2p_{1/2}$.

seven functionals. Therefore, in this work, we also tested such a procedure.

In ADF package, there are eight exchange (Becke88 [26], PW86x [2], PW91x [3], PBEx [27,28], RPBEx [29], revP-BEx [30], mPW91 [31], and OPTX [32]) and four correlation (Perdew86 [33,34], PBEc [27,28], PW91c [3], and LYP [35–37])

functionals. We tested 26 different combinations of exchange-correlation functionals out of all technically possible combinations.

3. Results

Table 2 presents the AAD values for the 2p CEBEs of the five elements (Si to Ar), resulted from the use of the best 18 functionals out of the 26 functionals tested. The values in parentheses in the table correspond to AADs calculated with the density obtained through the use of $V_{xc} = \text{SAOP}$. The AAD values for the Si in the table are the average for 56 molecules with experimental data [38] listed in Table 3 (Supplementary materials). Similarly, the AAD values for P, S, and Cl are the average for 28, 41, and 19 cases, respectively, and the experimental results of P, S, and Cl are presented, respectively, in Tables 4–6 (Supplementary materials). The experimental value we used for Ar (249.25 eV) is an average of observed values as listed in Table 1.

The last column lists weighed AAD averages that were calculated as $(56\text{Si} + 28\text{P} + 41\text{S} + 19\text{Cl} + 1\text{Ar})/145$. It provides information about the overall quality of each E_{xc} . The combination of OPTX-LYP (labelled A in Table 2), resulted the smallest weighted average of 0.26 eV and has the best overall quality as a functional for calculation of 2p CEBE of elements Si to Ar. A close second best is the OPTX-PBE functional (labelled B in Table 2), also with weighted average of 0.26 eV. However, in our judgment, the overall performance of OPTX-LYP is slightly superior to that of OPTX-PBE because the former has the smaller values of the AADs for the P, S, and Cl elements. There are seven E_{xc} functionals that resulted weighted average of less than 0.30 eV. The quality of calculated 2p CEBEs of Si to Ar elements of the seven functionals is roughly similar. As seen in the last column of Table 2, the use of SAOP resulted

almost identical weighted averages to those resulted through the use of E_{xc} with a few exceptions. In case of the best method, OPTX-LYP, for example, the weighted average calculated with E_{xc} is 0.26 eV, whereas that calculated through the use of SAOP is 0.27 eV. The only exceptions are the functionals PW91-PW91 and mPW91-PW91, where SAOP results are superiors to those of E_{xc} . Neither functional is among our top choices. Since the use of SAOP requires substantially more computing time than the use of E_{xc} and accuracy attained by the use of E_{xc} and SAOP are very similar for the most of the functionals tested, we recommend the use of E_{xc} for calculations of 2p CEBEs of the Si–Ar molecules, without getting the density from $V_{xc} = \text{SAOP}$ first.

The best overall functional OPTX-LYP is also the best E_{xc} for P- and Cl-containing molecules. For the other elements, however, other functionals lead to better prediction of 2p CEBEs. For some researchers who might be more interested in practical applications (than in finding theoretical reasons for the top choices), these individual functionals may be their best choice. In case of Si-containing molecules, the two best functionals are mPW91-PBE and Becke88-Perdew86 functionals, the AADs for which are only 0.10 eV, much smaller than 0.25 eV from the use of $E_{xc} = \text{OPTX-LYP}$. The best functionals for S are PBE-PW91 and PBE-Perdew86, both of which gave AADs of 0.32 eV, only marginally better than $E_{xc} = \text{OPTX-LYP}$. The best result for the Ar was obtained with the combination OPTX-Perdew86. Although that particular E_{xc} reproduced the observed value exactly, the agreement could be coincidental.

In Tables 3–6 (Supplementary materials), we present the results of 2p CEBE values (in eV) in various molecules containing Si, P, S, and Cl, respectively, calculated with these best functionals. Experimental values are listed in the last column of each table. The AADs corresponding to each of the various functionals are presented in the last line of the table.

Table 2
Average absolute deviations (in eV) for 145 cases (values from SAOP density given in parentheses)

E_x	E_c	AAD					Average
		Si	P	S	Cl	Ar	
OPTX	LYP	0.25 (0.27)	0.23 (0.23)	0.35 (0.36)	0.14 (0.14)	0.09 (0.08)	0.26 A (0.27)
OPTX	PBE	0.17 (0.19)	0.31 (0.30)	0.41 (0.42)	0.16 (0.17)	0.10 (0.03)	0.26 B (0.27)
mPW91	Perdew86	0.16	0.31	0.41	0.21	0.35	0.27
OPTX	PW91	0.23	0.28	0.39	0.19	0.03	0.28
PW91	Perdew86	0.12	0.36	0.45	0.24	0.41	0.28
OPTX	Perdew86	0.26	0.27	0.38	0.21	0.00	0.29
mPW91	PBE	0.10	0.40	0.49	0.28	0.46	0.29
mPW91	LYP	0.16	0.33	0.47	0.30	0.42	0.30
Becke88	Perdew86	0.10 (0.11)	0.43 (0.46)	0.52 (0.55)	0.31 (0.29)	0.49 (0.34)	0.31 (0.33)
PW91	LYP	0.12	0.38	0.52	0.35	0.49	0.32
PW91	PBE	0.13	0.46	0.53	0.32	0.52	0.33
Becke88	PW91	0.12 (0.13)	0.46 (0.48)	0.55 (0.56)	0.34 (0.32)	0.53 (0.37)	0.34 (0.34)
Becke88	LYP	0.12 (0.13)	0.45 (0.48)	0.59 (0.63)	0.43 (0.42)	0.57 (0.40)	0.36 (0.38)
PW86	PW91	0.19	0.55	0.69	0.53	0.75	0.45
PBE	PW91	0.75	0.35	0.32	0.26	0.14	0.48
PBE	Perdew86	0.75	0.35	0.32	0.27	0.14	0.48
PW91	PW91	0.91 (0.11)	0.49 (0.43)	0.42 (0.51)	0.44 (0.25)	0.33 (0.28)	0.63 (0.30)
mPW91	PW91	0.98 (0.13)	0.55 (0.36)	0.46 (0.46)	0.48 (0.22)	0.39 (0.22)	0.68 (0.28)

A = best overall method for Si to Ar; B = second best.

4. Discussions

Accurate calculation of 2p CEBEs for molecules containing the elements Si to Ar has not been easy. Cavigliasso [39] used an unrestricted generalized transition-state (uGTS) model to calculate 2p CEBEs of the third-period elements, Si, P, S, Cl, and Ar. For 22 test cases, the AAD obtained with uGTS model employing cc-pVTZ basis set was 0.84 eV. The size of the cc-pVTZ basis set is approximately equal to that of the TZP set used in the present study. Employing a much larger cc-pV5Z basis set, the AAD was reduced to 0.38 eV. More recently, Motozaki et al. [40] calculated 2p CEBEs of 11 Si- and 12 S-containing gas-phase molecules using unrestricted generalized diffuse ionization (uGDI) model with Becke88-Perdew86 functional and a newly designed scaled polarized valence triple-zeta basis set of CGTOs. The AAD obtained by the uGDI model for the 23 test molecules was 0.42 eV, which can be compared with the AAD value of 0.22 eV obtained with ΔE_{KS} (Becke88-Perdew86) procedure for the same set of test cases, and with the overall AAD of 0.26 eV for the 145 cases calculated with ΔE_{KS} (OPTX-LYP) protocol recommended in this work.

There are at least eight sources of error contributing to the AAD values:

- The procedure we recommend is based on a model we have been using since 1999, namely the assumptions that we can describe the core-hole cation by assigning occupation numbers to Kohn–Sham orbitals and that we can apply the variation method even though there is no variation principle for such a description. Such a model seems to work well for CEBEs.
- For 2p CEBE calculations, technical reasons have forced us to spread the 2p core-hole evenly to each of the three components. In other words, each of 2px, 2py, and 2pz orbitals shares one-third of the core hole.
- The treatment of relativistic effects by scalar-ZORA has been recommended for valence electrons. It was a pleasant surprise to us that the method seems to perform well for L-shell core-electrons as well.
- Undoubtedly, there is residual error in the functionals we have been using.
- The TZP basis set is far from the basis set limit. However, we have shown that increasing the size of the basis set from TZP has very little influence on the AAD for 1s CEBEs.
- The geometry used in this study, optimized by HF/6-31G(d) procedure may not be the best one to use. In the earlier study on 1s CEBEs of C to F, the choice of geometry was found to have only a small effect.
- There may be a small error in the approximate way in which we “normalize” experimental $2p_{3/2}$ values to $\langle 2p \rangle$ values for standard of comparison. The quality of this approximation may be estimated from inspection of Table 1.
- Finally, there is uncertainty in the experimental values reported in the literature. This can be seen from the different observed values reported by different researchers. Earlier results could easily be off by 0.1 eV, for example.

In our opinion, the largest contributors are (d and h). In spite of all the foregoing error sources, we are pleased to report that our recommended procedure ΔE_{KS} (OPTX-LYP) has performed well for 145 cases, with an AAD of only 0.26 eV, and that other choices of E_{xc} functionals can perform even better for individual elements in the series Si to Ar.

As long as the E_{xc} is among the top performers, the quality of the computed CEBEs is indeed only weakly dependent on the choice of functional. However, it should be noted that if an improper functional is used the value of AAD over the 145 cases can be much higher. It would be interesting to examine the difference between good and poor functionals to try to understand fundamental reason for the difference in performance, but such a project is beyond the scope of the present investigation.

5. Summary

Among 26 functionals tested for 145 cases in calculation of 2p core-electron binding energy of Si, P, S, Cl, and Ar, the best method was found to be:

$$\Delta E_{\text{KS}} (\text{scalar} - \text{ZORA} + \text{OPTX} - \text{LYP}) / \text{TZP} // \text{HF}/6 - 31\text{G(d)}.$$

Here, ΔE_{KS} is the difference in the total Kohn–Sham energies of the core-ionized cation and the neutral parent molecule calculated by DFT, using OPTX exchange and LYP correlation functionals, TZP basis set at the molecular geometry optimized with HF/6–31G(d). Relativistic effects are estimated by the scalar-ZORA method. The weighted AAD obtained for the 145 cases is 0.26 eV. A close second best choice is the use of the OPTX-PBE functional. There are seven E_{xc} functionals that resulted weighted average less than 0.30 eV (Table 2). The overall best OPTX-LYP functional gave also the best results for calculation of 2p CEBEs of P and Cl. But in case of Si, the best functionals are the combinations of either mPW91-PBE or Becke88-Perdew86, both of which resulted AADs of 0.10 eV for 56 molecules tested. In case of S, the two combinations, PBE-PW91 and PBE-Perdew86, give slightly more reliable CEBEs than $E_{\text{xc}} = \text{OPTX-LYP}$. Table 2 summarizes the performance of 18 functionals out of 26 tested for calculation of 2p CEBEs. The use of SAOP resulted almost identical weighted AADs to those resulted through the use of E_{xc} with a few exceptions. The proposed ΔE_{KS} (Becke88-Perdew86) model has shown superiority to the previous two models, uGTS and uGDI, in calculating 2p CEBEs of Si and S in gas molecules.

Acknowledgment

The authors thank Brazilian agency, Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for a research grant (# 2003/00075-9). MS thanks FAPESP for a scholarship (# 01/00794-0). YT thanks Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) of Brazil for a fellowship (# 300467/2003-6). DPC is grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support and FAPESP for a visiting fellowship (grant

2004/15849-2). Computational facilities were made available in Brazil by the Centro Nacional de Supercomputação no Rio Grande do Sul (CESUP-RS) and Centro Nacional de Computação de Alto Desempenho em São Paulo (CENAPAD-SP).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.elspec.2005.09.007](https://doi.org/10.1016/j.elspec.2005.09.007).

References

- [1] Y. Takahata, D.P. Chong, J. Electron Spectrosc. Relat. Phenom. 133 (2003) 69.
- [2] J.P. Perdew, Y. Wang, Phys. Rev. B: Condens. Matter Mater. Phys. 33 (1986) 8800.
- [3] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B: Condens. Matter Mater. Phys. 46 (1992) 6671.
- [4] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931.
- [5] D.P. Chong, J. Chem. Phys. 103 (1995) 1842.
- [6] W. Hayes, F.C. Brown, Phys. Rev. A: At. Mol. Opt. Phys. 6 (1972) 21.
- [7] P. Kelfve, B. Blomster, H. Siegbahn, K. Siegbahn, E. Sanhueza, O. Goscinski, Phys. Scr. 21 (1980) 75.
- [8] L. Cooper, L.G. Shpinkova, D.M.P. Holland, D.A. Shaw, Chem. Phys. 270 (2001) 363.
- [9] D. Pleul, R. Frenzel, M. Eschner, F. Simon, Anal. Bioanal. Chem. 375 (2003) 1276.
- [10] D.R. Beck, R.J. Key, A.R. Slaughter, R.D. Mathews, M.S. Banna, Phys. Rev. A: At. Mol. Opt. Phys. 28 (1983) 2634.
- [11] R.G. Cavell, Inorg. Chem. 14 (1975) 2828.
- [12] C.J. Allan, U. Gelius, D.A. Allison, G. Johansson, H. Siegbahn, K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. 1 (1972) 131.
- [13] L. Pettersson, J. Nordgren, L. Selander, C. Nordling, K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. 27 (1982) 29.
- [14] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne, Y. Baer, ESCA Applied to Free Molecules, North-Holland Publishing, Amsterdam, 1961.
- [15] M.S. Banna, D.C. Frost, C.A. McDowell, B. Wallbank, Chem. Phys. Lett. 43 (1976) 426.
- [16] E.J. Aitken, M.K. Bahl, K.D. Bomben, J.K. Gimzewski, C.S. Nolan, T.D. Thomas, J. Am. Chem. Soc. 102 (1980) 4873.
- [17] D.A. Allison, G. Johansson, C.J. Allan, U. Gelius, H. Siegbahn, J. Allison, K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. 1 (1972) 269.
- [18] T.D. Thomas, R.W. Shaw Jr., J. Electron Spectrosc. Relat. Phenom. 5 (1974) 1081.
- [19] M. Nakamura, M. Sasanuma, S. Sato, M. Watanabe, H. Yamashita, Y. Iguchi, A. Ejiri, S. Nakai, S. Yamaguchia, T. Sagawa, Y. Nakai, T. Oshio, Phys. Rev. Lett. 21 (1968) 1303.
- [20] G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, R. Nilsson, J. Electron Spectrosc. Relat. Phenom. 2 (1973) 295.
- [21] J. Nordgren, H. Ågren, C. Nordling, K. Siegbahn, Phys. Scr. 19 (1979) 5.
- [22] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, A.-M. Mårtensson-Pendrill, J. Phys. B: At. Mol. Phys. 19 (1986) 2799.
- [23] Ch. Chang, M. Pelissier, Ph. Durand, Phys. Scr. 34 (1986) 394.
- [24] E. van Lenthe, A.E. Ehlers, E.J. Baerends, J. Chem. Phys. 110 (1999) 8943.
- [25] P.R.T. Schipper, O.V. Gritsenko, S.J.A. van Gisbergen, E.J. Baerends, J. Chem. Phys. 112 (2000) 1344.
- [26] A.D. Becke, Phys. Rev. A: At. Mol. Opt. Phys. 38 (1988) 3098.
- [27] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [28] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
- [29] B. Hammer, L.B. Hansen, J.K. Nørskov, Phys. Rev. B: Condens. Matter Mater. Phys. 59 (1999) 7413.
- [30] Y. Zhang, W. Yang, Phys. Rev. Lett. 80 (1998) 890.
- [31] C. Adamo, V. Barone, J. Chem. Phys. 108 (1998) 664.
- [32] N.C. Handy, A.J. Cohen, Mol. Phys. 99 (2001) 403.
- [33] J.P. Perdew, Phys. Rev. B: Condens. Matter Mater. Phys. 33 (1986) 8822.
- [34] J.P. Perdew, Phys. Rev. B: Condens. Matter Mater. Phys. 34 (1986) 7406.
- [35] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys. 37 (1988) 785.
- [36] B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. 98 (1993) 5612.
- [37] T.V. Russo, R.L. Martin, P.J. Hay, J. Chem. Phys. 101 (1994) 7729.
- [38] W.L. Jolly, K.D. Bomben, C.J. Eyermann, At. Data Nucl. Data Tables 31 (1984) 433.
- [39] G. Cavaliasso, Master of Science Thesis, The University of British Columbia, 1999.
- [40] W. Motozaki, T. Otsuka, K. Endo, D.P. Chong, Polym. J. 36 (2004) 600.