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Benchmarking Approximate Density Functional Theory for s/d Excitation Energies in 3d Transition Metal Cations

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Abstract: Holthausen has recently provided a comprehensive study of density functional theory for calculating the s/d excitation energies of the 3d transition metal cations. This study did not include the effects of scalar relativistic effects, and we show here that the inclusion of scalar relativistic effects significantly alters the conclusions of the study. We find, contrary to the previous study, that local functionals are more accurate for the excitation energies of 3d transition metal cations than hybrid functionals. The most accurate functionals, of the 38 tested, are SLYP, PBE, BP86, PBELYP, and PW91.

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Key words: density functional theory; transition metals; relativistic effects

Introduction

A recent paper by Holthausen¹ benchmarked the accuracy of density functional theory^{2,3} (DFT) for the excitation energies, T_e , of 3d transition metal cations. The study is valuable because the ability of DFT to predict accurate excitation energies of transition metal compounds is an important issue in reactivity, functional nanotechnology, catalysis, and metalloenzyme mechanisms, as well as a subject of basic fundamental importance.^{4–25} The excitations are also of interest from a chemical standpoint, because the chemically bonded systems often have depopulated 4s states and enhanced 3d populations. The Holthausen¹ study had four main thrusts: (1) the technical and theoretical difficulties of calculating atomic T_e ; (2) a survey of several DFT methods using the TZVP²⁶ basis set, which resulted in a recommendation of the B3LYP^{27–30} functional; (3) a survey of the performance of several basis sets using the B3LYP functional; and (4) the influence of varying the fraction of Hartree–Fock exchange³¹ in the B3LYP functional, which indicated that little overall improvement is possible.

A recent paper by Balabanov and Peterson³² has shown that the scalar relativistic effects on the T_e values of neutral transition metal atoms are on the order of 3–9 kcal/mol, depending on the atom type. (The scalar relativistic effects tend to be larger for the atomic T_e values than for bond energies; in particular, the molecular systems they studied³² had scalar relativistic effects that were less than 3 kcal/mol for bond energies.) The Holthausen paper¹ included relativistic effects only by eliminating the spin-orbit effects (we call these vector relativistic

effects) from the experimental excitation energies, but it did not account for the scalar-relativistic effects. (Balabanov and Peterson³² also removed the spin-orbit effects from the experimental³³ numbers using experimental data.³³) Since the majority of the 38 density functionals studied by Holthausen had mean absolute deviations from experimental T_e values of 4.4–8.3 kcal/mol, the neglect of scalar relativistic effects is comparable to the errors caused by the inexactness of the functionals, and the conclusions bear re-examination. In this article, we show how including the scalar relativistic effects alters the conclusions.

Scalar Relativistic Effects

The scalar relativistic effect will be treated as an additive constant³⁴ here. The computed T_e will be calculated as

$$T_{e,\text{DFT,Rel}} = T_{e,\text{DFT,NRel}} + \Delta\text{SR} \quad (1)$$

where $T_{e,\text{DFT,Rel}}$ is the corrected excitation energy, $T_{e,\text{DFT,NRel}}$ is the excitation energy reported by Holthausen¹ for a DFT method with the TZVP basis set, and ΔSR is the scalar relativistic correction. The ΔSR values are taken from earlier work by Martin

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and Hay.³⁵ The scalar relativistic effect, ΔSR , is calculated from their results as

$$\Delta\text{SR} = T_{\text{e,Rel}} - T_{\text{e,NRel}} \quad (2)$$

where $T_{\text{e,Rel}}$ and $T_{\text{e,NRel}}$ are the excitation energies calculated with and without relativistic effects.

The Martin and Hay values³⁵ for ΔSR were calculated using numerical Hartree–Fock methods and the Cowan–Griffin³⁶ operator. The Hartree–Fock method is not a quantitatively accurate method for calculating T_{e} due to the neglect of electron correlation; however, the scalar relativistic effects mainly affect the core electrons, causing them to contract. The valence electrons are only indirectly affected because of the modification of their interaction with the core due to its contraction. It is not unreasonable to expect that the core contraction can be accounted for at the Hartree–Fock level. To test this, we will first compare the Hartree–Fock ΔSR values of Martin and Hay³⁵ to the coupled clusters ΔSR values of Balabanov and Peterson³² for the $4s^2 3d^{m-2} \rightarrow 4s^1 3d^{m-1}$ transition energy of the neutral 3d transition metal atoms to establish the accuracy of the Martin and Hay³⁵ Hartree–Fock ΔSR values. The ΔSR values for the neutral 3d transition metal atoms are given in Table 1. (The Hartree–Fock ΔSR values for the 3d cations are also given in Table 1 and will be discussed below.) The Balabanov–Peterson³² values for ΔSR of the neutrals were calculated at the coupled cluster theory with singles and double excitations and quasiperturbative triples,^{37–39} CCSD(T), complete basis set limit, CBS, with the Douglas–Kroll–Hess Hamiltonian^{40,41} for the relativistic effects. The Martin and Hay³⁵ values for ΔSR agree very well with the Balabanov–Peterson³² values for ΔSR . The mean unsigned error, MUE, for the Hartree–Fock ΔSR values is 0.07 kcal/mol, when compared to the CCSD(T)/CBS values. We conclude that the Martin and Hay method is reliable, and this justifies its use for the 3d cations for which the couple cluster values are not available.

The first row of Table 2 lists the experimental values of $\Delta E(4s^1 3d^{m-2} \rightarrow 3d^{m-1})$ for the 3d transition metal cations. Table 2

Table 1. ΔSR (in kcal/mol), for the $4s^2 3d^{m-2} \rightarrow 4s^1 3d^{m-1}$ Transition Energy of the Neutral 3d Transition Metal Atoms and the $4s^1 3d^{m-2} \rightarrow 3d^{m-1}$ Excitation Energy of the 3d Transition Metal Cations.

Atom	Neutral		Cation
	CCSD(T)/CBS	HF	HF
Sc	2.69	2.77	3.69
Ti	3.30	3.23	3.92
V	3.94	3.92	5.07
Cr	4.84	4.84	6.00
Mn	4.62	4.61	6.23
Fe	5.92	6.00	7.38
Co	7.01	6.92	8.53
Ni	8.16	8.30	9.22
Cu	9.73	9.92	10.38
MUE		0.07	

also contains $T_{\text{e,DFT,Rel}}$ values calculated by Eq. (1) using the Holthausen values for $T_{\text{e,DFT,NRel}}$ and the Martin–Hay values for ΔSR as described above. The Holthausen¹ values corresponds to excitation energies T_{e} out of the ground electronic state for the cation. The ground states of the Sc, Ti, Mn, and Fe cations are $4s^1 3d^{m-2}$, and the ground states for the V, Cr, Co, Ni, and Cu cations are $3d^{m-1}$. Thus, $\Delta E = T_{\text{e}}$ for Sc, Ti, Mn, and Fe, and these values are adjusted by ΔSR , whereas ΔE for V, Cr, Co, Ni, and Cu is adjusted by $-\Delta\text{SR}$. Also, the T_{e} value for V^+ listed by Holthausen¹ is 6.90 kcal/mol, but the value obtained from the tabulation of Moore³³ is 7.90 kcal/mol. (The spin-orbit effects have been removed from the experimental number using the same method as Holthausen.¹) We assume that this was a simple data error in Holthausen’s work, and we use the value from Moore. In addition to 38 density functionals, Table 2 also includes results for Hartree–Fock (HF) and CCSD(T). The last column of Table 2 also lists two error quantities, MUE(Rel) and MUE(NRel). The MUE(NRel) are recomputed using correct value for $T_{\text{e}}(\text{V}^+)$ and the DFT values without the scalar relativistic corrections. MUE(Rel) is computed using the correct value for $T_{\text{e}}(\text{V}^+)$, and the DFT values with the scalar relativistic corrections.

The main point that we wish to make in this note is that the inclusion of scalar-relativistic effects changes the conclusions as to which group of functionals is the most accurate. An important qualitative conclusion that would be drawn from Holthausen’s work is that hybrid functionals are more accurate than local functionals. In particular, the MUE(NRel) values for B1LYP, B3LYP, mPW1PW91, and PBE1PBE functionals are less than the MUE(NRel) values for their nonhybrid counterparts, BLYP, BLYP, mPWPW91, and PBE, respectively. However, the MUE(Rel) values for the BLYP,^{27,28} mPWPW91,^{42,43} and PBE⁴⁴ are smaller than their hybrid counterparts. Thus, the

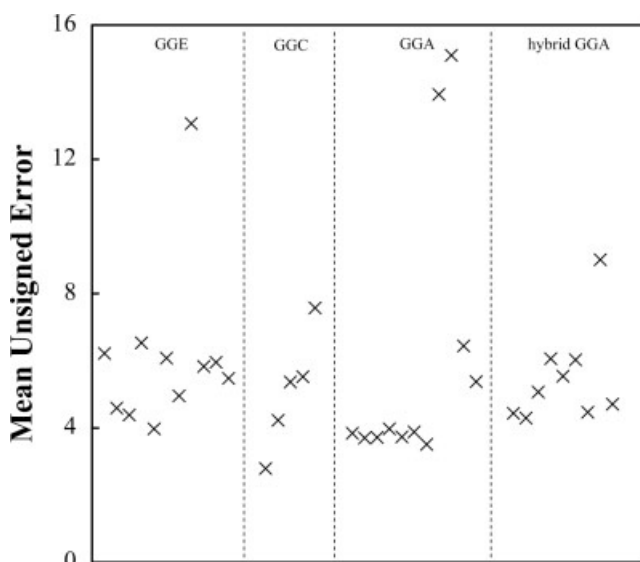


Figure 1. The MUE, in kcal/mol, in excitation energies for the GGE, GGC, GGA, and hybrid GGA functionals. The order of the functionals along the abscissa is the same as in Table 2.

Table 2. Experimental and Computed T_e Values in kcal/mol.

Method ^a	X ^b	Sc ⁺	Ti ⁺	V ⁺	Cr ⁺	Mn ⁺	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺	MUE	
											Rel	NRel
Exp ^c		13.8	2.3	7.9	35.1	41.7	5.8	9.9	24.9	64.8		
HF	100	22.8	14.7	−8.8	20.4	85.8	48.2	−37.1	−26.2	19.9	31.4	24.5
CCSD(T)	100	20.3	8.6	0.6	32.4	62.1	22.9	−7.7	7.0	57.5	11.5	6.1
S	0	19.6	7.3	2.8	30.2	68.4	31.0	−10.6	8.1	54.7	13.3	7.1
X α	0	14.1	1.2	9.5	37.5	65.2	26.4	−4.9	14.9	62.3	8.5	7.8
SVWN	0	7.0	−5.1	15.1	42.1	36.9	2.7	14.4	30.5	74.4	6.2	13.1
SVWN5	0	7.9	−4.4	14.5	41.7	39.5	5.4	11.9	28.2	72.5	4.6	11.4
SVWN-50	0	13.4	1.2	8.9	36.1	52.7	16.8	1.9	19.3	64.5	4.4	5.1
SVWN-35	0	15.3	3.0	7.0	34.3	57.4	21.1	−1.8	15.9	61.6	6.5	4.9
BLYP	0	7.2	−1.2	6.6	34.9	34.4	3.1	7.1	16.5	61.8	4.0	7.3
BVWN	0	2.8	−5.0	10.0	37.9	28.7	−3.7	13.9	22.8	67.7	6.1	12.4
BVWN5	0	3.7	−4.3	9.4	37.5	31.3	−1.0	11.4	20.6	65.8	5.0	10.8
OVWN	0	−4.2	−14.3	21.5	50.8	28.8	−5.2	19.0	31.7	78.7	13.1	19.9
PW91VWN	0	3.7	−4.1	9.5	37.9	28.7	−3.7	13.7	22.8	68.0	5.8	12.2
mPW91VWN	0	3.2	−4.6	9.7	37.9	28.7	−3.7	13.7	22.6	67.7	6.0	12.2
PBEVWN	0	4.5	−3.6	9.2	37.6	29.2	−3.2	13.5	22.7	67.8	5.5	11.8
SLYP	0	11.4	−1.3	11.7	39.1	42.6	9.4	7.6	24.2	68.5	2.8	7.9
SP86	0	10.0	−3.4	14.6	41.3	44.6	10.0	8.7	26.5	70.5	4.2	9.2
SPW91	0	8.6	−4.7	15.7	42.7	47.3	11.8	7.7	25.9	70.7	5.4	9.1
SPBE	0	8.5	−4.8	15.9	42.9	47.7	12.1	7.6	25.9	70.7	5.5	9.1
OLYP	0	0.4	−10.2	17.8	47.5	34.9	2.0	11.7	25.0	72.3	7.6	14.4
PW91LYP	0	8.1	−0.3	6.1	34.9	34.5	3.1	6.8	16.4	62.0	3.8	7.0
PBELYP	0	8.8	0.2	5.8	34.6	35.0	3.7	6.6	16.4	61.8	3.7	6.7
BP86	0	5.8	−3.3	9.5	37.1	36.4	3.7	8.2	18.8	63.8	3.7	8.6
BPW91	0	4.4	−4.6	10.7	38.6	39.1	5.5	7.2	18.2	64.0	4.0	8.5
PW91	0	5.3	−3.7	10.1	38.6	39.1	5.4	6.9	18.1	64.2	3.7	8.3
mPWPW91	0	4.8	−4.1	10.3	38.5	39.1	5.4	6.9	18.0	64.0	3.9	8.3
PBE	0	6.0	−3.3	10.0	38.4	40.0	6.2	6.6	18.2	64.1	3.5	7.9
HCTH93	0	−3.5	−15.4	24.4	54.0	33.3	−2.9	19.7	35.5	82.3	13.9	20.8
HCTH407	0	−4.4	−16.8	26.3	55.7	31.3	−4.1	19.9	36.3	82.7	15.1	21.9
VSXC	0	2.9	−9.6	15.8	47.0	44.6	8.2	11.7	24.1	72.3	6.4	11.9
TPSS	0	1.7	−2.9	8.2	37.8	37.1	2.1	3.7	14.1	62.0	5.4	8.1
B3LYP	20	8.1	−0.5	6.4	34.6	39.2	7.1	3.2	13.0	57.7	4.4	5.4
B3P86	20	5.7	−3.5	10.0	37.6	39.8	6.5	5.3	16.1	60.6	4.3	7.0
B3PW91	20	5.9	−3.2	9.7	37.7	43.2	9.2	3.1	14.2	59.4	5.1	6.0
B97-1	21	4.3	−4.3	10.2	38.7	34.8	−0.1	11.1	21.1	65.2	4.5	10.4
B97-2	21	0.1	−10.0	17.1	46.2	33.0	−2.8	16.0	28.2	72.9	9.0	15.8
B98	21.98	3.7	−5.0	11.1	39.6	35.1	0.4	10.8	21.2	65.5	4.7	10.7
mPW1PW91	25	6.3	−2.7	9.0	37.3	45.3	11.0	0.8	11.7	57.2	6.1	5.3
B1LYP	25	9.0	0.6	5.0	33.3	40.9	9.1	0.5	9.8	54.6	5.5	4.4
PBE1PBE	25	7.2	−2.0	8.8	37.1	46.1	11.7	0.5	11.8	57.2	6.0	4.9

The DFT values were computed with the TZVP basis set and have been adjusted for scalar relativistic effects. The MUEs are computed for the DFT methods with and without the scalar relativistic effects included.

^aRefer to ref. 1 for the appropriate literature references for methods not discussed in the text.

^bPercentage of Hartree-Fock exchange.

^cJ-average values taken from ref. 9.

opposite conclusion is drawn if scalar relativistic effects are included.

Furthermore, the conclusions about which specific functionals are best also change. Holhausen concluded that the B1LYP,^{27,28,45} B3LYP, mPW1PW91,^{42,43} and PBE1PBE^{44,46} functionals perform the best of the standard functionals that he tested, and due to the great deal of experience that has been gained with B3LYP, he recommends it for quantitative work. However, the functional with the lowest MUE(Rel), 2.8 kcal/

mol, of all the methods tested is SLYP,^{28,47} which is a nonstandard functional that uses the local exchange functional of Slater⁴⁷ and the gradient corrected functional of Lee et al.²⁸ The method with the second lowest MUE(Rel), 3.5 kcal/mol, is PBE. The BP86,^{27,48} PW91,⁴⁹ PBELYP,^{28,44} PW91LYP,^{28,49} and mPWPW91⁴² functionals also have errors of less than 4.0 kcal/mol. The seven functionals singled out so far and in fact all of the ten best functionals in Table 2 are GGA functionals, which is consistent with previous studies.^{50,51} Of the hybrid methods

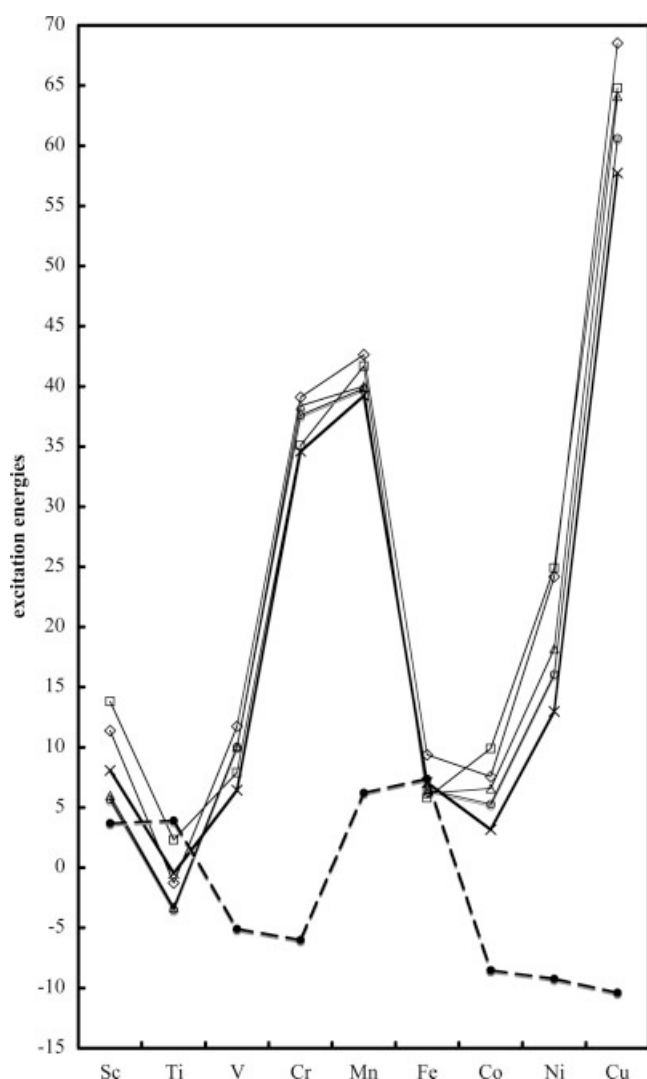


Figure 2. The experimental excitation energies (\square) and the excitation energies computed with SLYP (\diamond), PBEPBE (\triangle), B3P86 (\circ), and B3LYP (\times) for the 3d transition metal cations. The scalar relativistic effect, ΔSR , is also plotted with a dashed line and solid circles. The units for the plot are kcal/mol.

tested, the B3P86 method has the lowest MUE(Rel), 4.3 kcal/mol. The B3LYP method is still one of the more reasonable methods studied, but it is not among the eleven best functionals; the MUE(Rel) of B3LYP is 4.4 kcal/mol, which is 0.4 kcal/mol larger than BLYP. To provide a different perspective than mean unsigned errors, Figure 1 plots the excitation energies for SLYP, PBEPBE, B3P86, and B3LYP. (We also plot the experimental excitation energies and ΔSR in Figure 2.) All of the functionals seem to show the same general trends, and we have found that the MUE is the best diagnostic for evaluating functional performance.

For 32 of the 38 density functionals in Table 2, the mean error is smaller when scalar relativistic effects are included than when they are not. In 15 cases, the mean error decreases by

more than a factor of two. Therefore, it is very dangerous to study these excitation energies without including scalar relativistic effects. In this work, the scalar relativistic effects were treated as constants, but the computationally simplest way to treat them is with relativistic effective core potentials.^{52,53} The error in the 19th best functional (and therefore in the majority of the functionals tested) has decreased from 8.3 kcal/mol to 5.4 kcal/mol.

Conclusions

We have reanalyzed the recommendations made by Holthausen¹ for the excitation energies of 3d transition metal cations. If the scalar relativistic effects are not included, as in the work of Holthausen, the hybrid functionals tend to be more accurate than the local functionals. In this comment, we have made additive corrections for the scalar-relativistic effects, and we found that the nonhybrid functionals are more accurate than the hybrid functionals when scalar relativistic effects are included. The two most accurate functionals are SLYP and PBE, with mean unsigned errors of 2.8 and 3.5 kcal/mol, respectively.

References

- Holthausen, M. C. *J Comp Chem* 2005, 26, 1505.
- Kohn, W.; Becke, A. D.; Parr, R. G. *J Phys Chem* 1996, 100, 12974.
- Kohn, W. *Rev Mod Phys* 1998, 71, 1253.
- Lovell, T.; Stranger, R.; McGrady, J. E. *Inorg Chem* 2001, 40, 39.
- Reiher, M.; Saloman, O.; Hess, B. A. *Theor Chem Acc* 2001, 107, 48.
- Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Cabollol, R. J. *J Chem Phys* 2002, 116, 3985.
- Saloman, O.; Reiher, M.; Hess, B. A. *J Chem Phys* 2002, 117, 4729.
- Harvey, J. N.; Poli, R.; Smith, K. M. *Coord Chem Rev* 2003, 238/239, 347.
- Schoneboom, J. C.; Cohen, S.; Lin, H.; Shaik, S.; Theil, W. *J Am Chem Soc* 2004, 126, 4017.
- Carreon-Macedo, J.-L.; Harvey, J. N. *J Am Chem Soc* 2004, 126, 5789.
- Poli, R. *J Organomet Chem* 2004, 689, 4291.
- Hermann, C.; Neugebauer, J.; Gladysz, J. A.; Reiher, M. 2005, 44, 6174.
- Jenkins, D. M.; Peters, J. C. *J Am Chem Soc* 2005, 127, 7148.
- Neese, F. *J Inorg Biochem* 2006, 100, 716.
- Carreon-Macedo, J.-L.; Harvey, J. N. *Phys Chem Chem Phys* 2006, 8, 93.
- Mehn, M. P.; Brown, S. D.; Paine, T. K.; Brennessel, W. W.; Cramer, C. J.; Peters, J. C.; Que, L. J. *Dalton Trans* 2006, 2006, 1347.
- Rudra, I.; Wu, Q.; Van Voorhis, V. *J Chem Phys* 2006, 124, 24103.
- Takano, Y.; Kitigawa, Y.; Onishi, T.; Yoshioka, Y.; Yamaguchi, K.; Koga, N.; Iwamura, H. *J Am Chem Soc* 2006, 124, 450.
- Bachler, V.; Olbrich, G.; Neese, F.; Weyherhardt, K. *Inorg Chem* 2002, 41, 4179.
- Lovell, T.; Torres, R. A.; Han, W.-G.; Liu, T.; Case, D. A.; Noodleman, L. *Inorg Chem* 2002, 41, 5244.
- Ghosh, P.; Bill, E.; Weyhermüller, T.; Neese, F.; Weyherhardt, K. *J Am Chem Soc* 2003, 125, 1293.
- Lovell, T.; Him, F.; Han, W.-G.; Noodleman, L. *Coord Chem Rev* 2003, 238/239, 211.

23. O'Brien, T. A.; Davidson, E. R. *Int J Quantum Chem* 2003, 92, 294.
24. Sinnecker, S.; Neese, F.; Noodleman, L.; Lubitz, W. *J Am Chem Soc* 2004, 126, 2613.
25. Beñard, M.; Berry, J. F.; Co Hon, F. A.; Gaudin, C.; Lopez, X.; Murillo, C. A.; Rohmer, M.-M. *Inorg Chem* 2006, 45, 3932.
26. Schäfer, A.; Huber, C.; Ahlrichs, R. 1994, 100, 5829.
27. Becke, A. D. *Phys Rev A* 1988, 38, 3098.
28. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
29. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J Phys Chem* 1994, 98, 11623.
30. Becke, A. D. *J Chem Phys* 1993, 98, 5648.
31. Becke, A. D. *J Chem Phys* 1993, 98, 1372.
32. Balabanov, N. B.; Peterson, K. A. *J Chem Phys* 2005, 123, 064107.
33. Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards, U.S. Government Printing Office: Washington, DC, 1949.
34. Martin, J. M. L.; Sundermann, A.; Fast, P. L.; Truhlar, D. G. *J Chem Phys* 2000, 113, 1348.
35. Martin, R. L.; Hay, P. J. *J Chem Phys* 1981, 75, 4539.
36. Cowan, R. D.; Griffin, D. C. *J Opt Soc Am* 1976, 66, 1010.
37. Čížek, J. *Adv Chem Phys* 1969, 14, 35.
38. Purvis, G. D.; Bartlett, R. J. *J Chem Phys* 1982, 76, 1910.
39. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem Phys Lett* 1996, 157, 479.
40. Douglas, M.; Kroll, N. M. *Ann Phys (NY)* 1974, 82, 89.
41. Hess, B. A. *Phys Rev A* 1989, 39, 6016.
42. Adamo, C.; Barone, V. *J Chem Phys* 1998, 108, 664.
43. Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P.; Esching, H., Eds.; Akademie Verlag: Berlin, 1991.
44. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys Rev Lett* 1996, 77, 3865.
45. Adamo, C.; Barone, V. *Chem Phys Lett* 1997, 274, 242.
46. Adamo, C.; Cossi, M.; Barone, V. *THEOCHEM* 1999, 493, 145.
47. Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974.
48. Perdew, J. P. *Phys Rev B* 1986, 33, 8822.
49. Perdew, J. P.; Wang, Y. *Phys Rev B* 1992, 98, 1372.
50. Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J Phys Chem A* 2005, 109, 4388.
51. Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J Phys Chem A* 2005, 109, 11127.
52. Krauss, M.; Stevens, W. J. *Annu Rev Phys Chem* 1984, 35, 357.
53. Schultz, N. E.; Gherman, B. F.; Cramer, C. J.; Truhlar, D. G. *J Phys Chem A* 2006, 110, 24030.