10º SIMPÓSIO DE ESTRUTURA ELETRÔNICA & DINÂMICA MOLECULAR
SEED MOL
4 a 8 novembro | 2024
Pirenópolis, Goiás

Complete basis set extrapolations using the new relativistic prolapse-free Gaussian basis sets of the RPF-XZ family (X = 2, 3, and 4)

Roberto Luiz Andrade Haiduke[1]
[1]Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador São-Carlense, 400, 13560-970, São Carlos, SP, Brazil.
haiduke@iqsc.usp.br

Keywords: variational prolapse; complete basis set extrapolations; relativistic calculations; double ionization potentials.

Abstract

Complete basis set extrapolations are successfully used with the new relativistic prolapse-free Gaussian basis sets, RPF-XZ (X = 2, 3, and 4), in four-component Coupled Cluster Theory calculations with single, double and perturbative triple substitutions for double ionization energy determinations in simple atomic systems.

Introduction

Important relativistic effects in chemistry are frequently encountered in different properties [1]. However, the electronic structure treatments based on the four-component formalism, which is one of the most advanced methodologies to include such effects, require specifically tailored basis sets. However, these basis sets can suffer from variational prolapse, which is an incompleteness issue associated to a poor description of inner electrons that can lead to smaller energy results than the exact values [2,3]. Hence, basis sets with variational prolapse are not recommended for calculations of properties more dependent on inner electron distributions. A few years ago, relativistic prolapse-free Gaussian basis sets of quadruple-ζ quality (RPF-4Z) were developed [4-6]. Our research group is now working on generating double- and triple-ζ quality members of the RPF-XZ family, which is almost finished for *s* and *p*-block elements [7].

Thus, Complete Basis Set (CBS) extrapolation schemes can be used to achieve more accurate electronic energies by carrying out calculations with basis sets of different sizes within a family [8]. However, considering relativistic calculations, it is mandatory to address the variational prolapse problem before extrapolations are employed or else the electronic energies will inevitably lead to wrong absolute results, which can will tend to be significantly smaller than the exact values.

Here, the RPF-XZ family (X = 2, 3, and 4) will be used to achieve extrapolated CBS results including high level treatments for relativistic effects and electronic correlation in order to obtain double ionization energies for some closed shell atoms (He, Be, Mg, Ca, Sr, Ba, and Ra).

Methodology

The Dirac-Coulomb (DC) Hamiltonian was used in all calculations, which are performed with DIRAC23 [9,10]. The default Gaussian nuclear model and light speed value are used. Uncontracted basis sets are considered here. Moreover, repulsion integrals between *small* functions generated by kinetic balance conditions, (SS|SS), are replaced for an approximation [11]. The energy results are obtained in four-component Coupled Cluster Theory calculations with single, double and perturbative triple excitations, DC-CCSD(T), with an active space composed by valence plus sub-valence electrons and virtual spinors up to 100 atomic units (*au*).

Two common extrapolation equations [12,13] are evaluated here for obtaining CBS results for energies (E_{CBS}):

$$E(X)=E_{CBS}+AX^{-3} \quad \text{or} \qquad (1)$$

$$E(X)=E_{CBS}+A(X+½)^{-4}\ , \qquad (2)$$

where $E(X)$ represents the energy obtained with a basis set of a certain cardinal number (X = 2, 3, and 4 for the RPF-XZ family) and A is a parameter. Thus, these CBS estimates require two calculations.

Results and Discussion

The double ionization process investigated here is based on calculations for closed-shell systems, a neutral atom and its double cation (A and A^{2+}), that is:

$$A \rightarrow A^{2+} + 2e^{-} \qquad (3)$$

Hence the total energies of A and A^{2+} are obtained by the extrapolations presented in eqs. (1) and (2). Thus, the double ionization results are compared to experimental data [14]. Table I illustrates the mean absolute deviations (MADs) and mean signed errors (MSEs) obtained with the RPF-XZ basis sets. As one can see, there is a clear improvement pattern as the cardinal number increases, with MADs decreasing from 0.23 to 0.08 eV, although the calculations always underestimate the double ionization data.

In the sequence, the CBS extrapolations are considered in Table II. Hence, the results are obtained from pairs of basis sets, that is, the pairs formed by the smallest and the largest sets, labelled respectively as (2Z,3Z) and (3Z,4Z). As one can notice, the (2Z,3Z) values from CBS extrapolations point to a clear improvement in the overall results individually obtained from the smallest basis sets, with MADs (around 0.09 and 0.10 eV) and MSEs (nearby -0.09 and -0.10 eV) similar to those from the RPF-4Z set. Further, the best MADs (0.05 eV) and MSEs (around -0.04 and -0.05 eV) are those from (3Z,4Z) CBS extrapolations.

Table I: Results obtained for double ionization energies in DC-CCSD(T) calculations and experimental data (in eV).

	RPF-2Z	**RPF-3Z**	**RPF-4Z**	**Exp**[a]
He	78.72	78.91	78.98	79.01
Be	27.50	27.51	27.52	27.53
Mg	22.34	22.43	22.57	22.68
Ca	17.82	17.88	17.93	17.98
Sr	16.52	16.59	16.63	16.73
Ba	15.05	15.08	15.09	15.22
Ra	15.03	15.26	15.29	15.43
MAD	0.23	0.13	0.08	
MSE	-0.23	-0.13	-0.08	

[a] From reference [14].

Table II: Results obtained for double ionization energies in DC-CCSD(T)/CBS calculations (in eV).

	(2Z,3Z)		**(3Z,4Z)**	
	eq. (1)	**eq. (2)**	**eq. (1)**	**eq. (2)**
He	79.00	78.98	79.04	79.02
Be	27.51	27.51	27.53	27.53
Mg	22.46	22.46	22.67	22.64
Ca	17.91	17.91	17.97	17.96
Sr	16.63	16.62	16.66	16.66
Ba	15.10	15.09	15.10	15.10
Ra	15.35	15.33	15.31	15.31
MAD	0.09	0.10	0.05	0.05
MSE	-0.09	-0.10	-0.04	-0.05

Conclusions

The results obtained here demonstrate that the RPF-XZ family (X = 2, 3, and 4) of relativistic Gaussian basis sets can be successfully used in CBS extrapolation schemes.

Acknowledgements

The author is grateful to São Paulo Research Foundation (FAPESP) for financial support (2022/05138-0). The funding from National Council for Scientific and Technological Development (CNPq) is also acknowledged (306763/2021-4).

References

[1] Pyykkö, P. *Annu. Rev. Phys. Chem.* 2012, 63, 45.

[2] Faegri Jr, K. *Theor. Chem. Acc.* 2001, 105, 252.

[3] Tatewaki, H.; Mochizuki, Y. *Theor. Chem. Acc.* 2003, 109, 40.

[4] Teodoro, T.Q.; da Silva, A.B.F.; Haiduke, R.L.A. *J. Chem. Theory Comput.* 2014, 10, 3800.

[5] Teodoro, T.Q.; da Silva, A.B.F.; Haiduke, R.L.A. *J. Chem. Theory Comput.* 2014, 10, 4761.

[6] Teodoro, T.Q.; Visscher, L.; da Silva, A.B.F.; Haiduke, R.L.A. *J. Chem. Theory Comput.* 2017, 13, 1094.

[7] Sousa, J.S.; Gusmão, E.F.; Dias, A.K.N.R., Haiduke, R.L.A. 2024, in preparation.

[8] Feller, D. *J. Chem. Phys.* 1992, 96, 6104.

[9] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC23 (2023), written by Bast, R.; Gomes, A.S.P.; Saue, T.; Visscher, L.; Jensen, H. J. Aa. with contributions from several authors (https://doi.org/10.5281/zenodo.7670749, see also https://www.diracprogram.org).

[10] Saue, T.; Bast, R.; Gomes, A.S.P.; Jensen, H.J.A.; Visscher, L.; Aucar, I.A.; Di Remigio, R.; Dyall, K. G.; Eliav, E.; Fasshauer, E.; Fleig, T.; Halbert, L.; Hedegård, E.D.; Helmich-Paris, B.; Iliaš, M.; Jacob, C.R.; Knecht, S.; Laerdahl, J.K.; Vidal, M.L.; Nayak, M.K.; Olejniczak, M.; Olsen, J.M.H.; Pernpointner, M.; Senjean, B.; Shee, A.; Sunaga, A.; van Stralen, J.N.P. *J. Chem. Phys.* 2020, 152, 204104.

[11] Visscher, L. *Theo. Chem. Acc.* 1997, 98, 68.

[12] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* 1997, 106, 9639.

[13] Martin, J.M.L. *Chem. Phys. Lett.* 1996, 259, 669.

[14] Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2023). NIST Atomic Spectra Database (version 5.11), [Online]. Available: https://physics.nist.gov/asd [Fri Aug 02 2024]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W30F