INSIGHT ON GAUSSIAN BASIS SET TRUNCATION ERRORS IN WEAK TO INTERMEDIATE MAGNETIC FIELDS

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Outline

1. Regions of magnetic field strengths
   - Weak
   - Intermediate
   - Strong
2. Research question: Can we tailor GTO basis sets for intermediate magnetic fields?
3. Methods: GTOs vs fully numerical basis set
4. Results
   - Performance of GTO basis sets
   - Standard basis sets vs benchmark quality sets
5. Summary
6. Future work

Weak region

- $|B| \approx 0$
- Zero-field symmetry
- Basis sets optimized at zero-field work well
- Coulomb interactions dominate
- The magnetic field is a perturbation

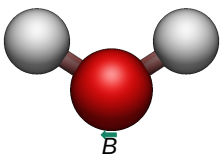

Figure: The electronic structure is barely affected in the weak region.

Strong region

- $B \gg B_0$
- Needle-like orbitals and molecular chains
- Ground state is fully spin polarized
- Coulomb interaction is a perturbation compared to the magnetic field

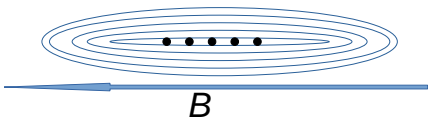

Figure: In the strong region the symmetry is extremely deformed.

Intermediate region

- $|B| = \mathcal{O}(B_0)$
- Rich chemistry

A Paramagnetic Bonding Mechanism for Diatomics in Strong Magnetic Fields

Kai K. Lange,[1] E. I. Tellgren,[1] M. R. Hoffmann,[1,2] T. Helgaker[1]*

A DZ white dwarf with a 30 MG magnetic field

M. A. Hollands [1]★ S. Stopkowicz [2,3,4] M.-P. Kitsaras [3] F. Hampe,[3] S. Blaschke [3] and J. J. Hermes [5]

Intermediate region

$$H = H_0 + \frac{1}{2}BL_z + BS_z + \frac{1}{8}B^2(x^2 + y^2) \tag{1}$$

- Different spin orbitals couple to the magnetic field differently via L_z and S_z
- Choice of basis set requires extra care!
- Large basis set truncation errors (BSTEs) for molecules[1]
- Can the root of the problem be found in atomic calculations?

1. Lehtola, S.; Dimitrova, M.; Sundholm, D. Mol. Phys. **2020**, 118, e1597989

Research questions

- How do the low lying states of the H–Ar atoms evolve as a function of B?
- Are these states the source for the BSTEs for standard GTO basis sets?
- Can we capture the magnetic field induced effects with a suitable GTO expansion?

Endgame: Tailor GTO basis sets for specifically optimized intermediate magnetic fields

Gaussian basis sets

Basis functions have the form

$$\psi_{nlm}(\mathbf{r}) = [r^l e^{-\alpha_{nl}\mathbf{r}^2}] Y_{lm}(\vartheta, \varphi) \tag{2}$$

which are:

- Globally defined $\rightarrow$ less flexible than finitely supported basis sets
- $Y_{lm}(\vartheta, \varphi) : S^2 \rightarrow \mathbb{R}$

Gaussian basis sets

unc-cc-pVDZ
unc-cc-pVTZ
unc-cc-pVQZ
unc-cc-pV5Z
unc-aug-cc-pVDZ
unc-aug-cc-pVTZ
unc-aug-cc-pVQZ
unc-aug-cc-pV5Z

unc-6-311++G(3df,3dp)
unc-def2-TZVP

HGBSP1-5 AHGBSP1-5
HGBSP1-7 AHGBSP1-7
HGBSP1-9 AHGBSP1-9
HGBSP2-5 AHGBSP2-5
HGBSP2-7 AHGBSP2-7
HGBSP2-9 AHGBSP2-9
HGBSP3-5 AHGBSP3-5
HGBSP3-7 AHGBSP3-7
HGBSP3-9 AHGBSP3-9

The HGBS basis sets

Polarized Gaussian basis sets from one-electron ions

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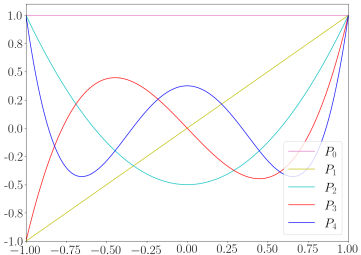
Susi Lehtola[a)]

Numerical basis sets

$$\psi_{nlm}(\mathbf{r}) = r^{-1} B_n(r) Y_l^m(\vartheta, \varphi) \tag{3}$$

- Locally defined $\rightarrow$ flexible
- $Y_l^m(\vartheta, \varphi) : S^2 \rightarrow \mathbb{C}$



Numerical basis sets

We can obtain exact energies at the CBS limit

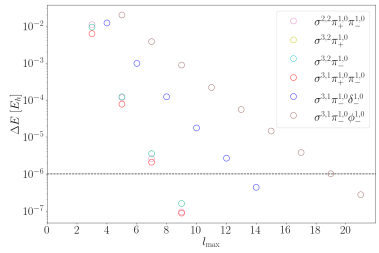


Figure: Convergence of the energy of low lying configurations of the C atom with respect to the basis set.

Results

Insight on Gaussian Basis Set Truncation Errors in Weak to Intermediate Magnetic Fields with an Approximate Hamiltonian

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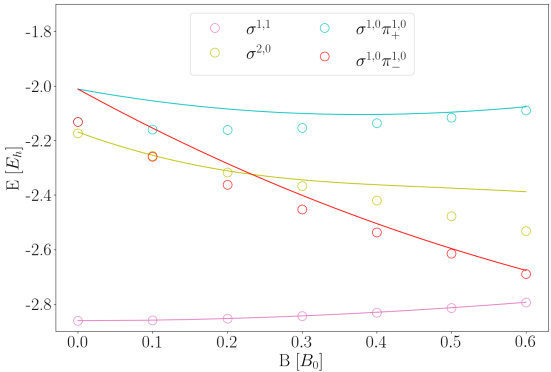
Hugo Åström and Susi Lehtola*

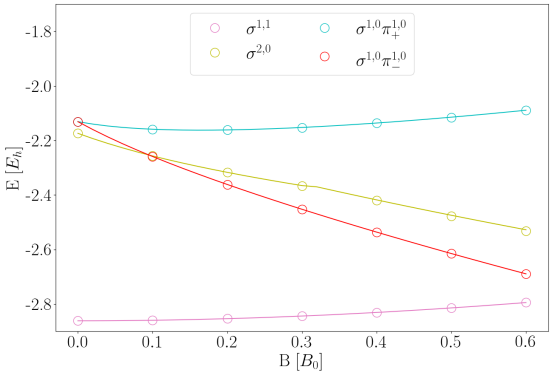
Results

Low lying states of the He atom in the unc-aug-cc-pVTZ basis set.



Results

Low lying states of the He atom in the AHGBSP3-9 basis set.



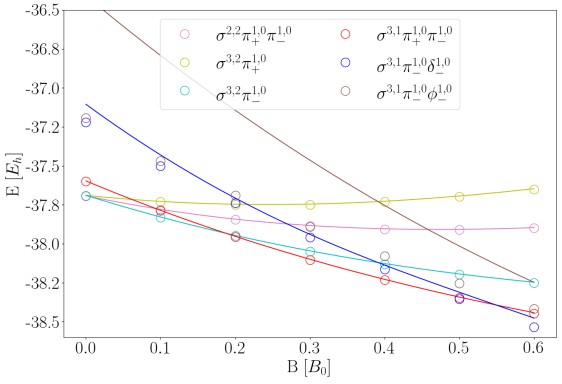
Results

	state	unc-aug-cc-pVTZ	AHGBSP3-9
0	$\sigma^{1,1}$	0.635	0.000
1	$\sigma^{2,0}$	48.331	1.401
2	$\sigma^{1,0}\pi_{+}^{1,0}$	59.467	0.266
3	$\sigma^{1,0}\pi_{-}^{1,0}$	59.467	0.266

Mean average energy differences between GTO and FEM energies in mE_h for He in the unc-aug-cc-pVTZ and AHGBSP3-9 basis sets.

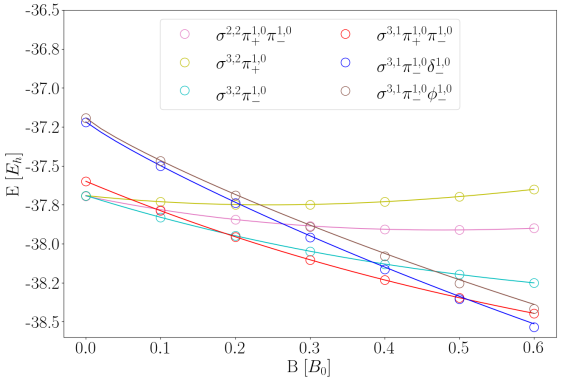
Results

Low lying states of the C atom in the unc-aug-cc-pVTZ basis set.



Results

Low lying states of the C atom in the AHGBSP3-9 basis set.



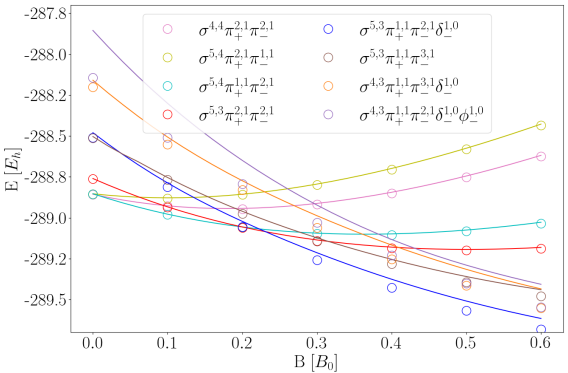
Results

	state	unc-aug-cc-pVTZ	AHGBSP3-9
0	$\sigma^{2,2}\pi_+^{1,0}\pi_-^{1,0}$	2.761	0.006
1	$\sigma^{3,2}\pi_+^{1,0}$	2.714	0.016
2	$\sigma^{3,2}\pi_-^{1,0}$	2.714	0.016
3	$\sigma^{3,1}\pi_+^{1,0}\pi_-^{1,0}$	3.288	0.015
4	$\sigma^{3,1}\pi_-^{1,0}\delta_-^{1,0}$	51.333	9.391
5	$\sigma^{3,1}\pi_-^{1,0}\phi_-^{1,0}$	452.152	12.204

Mean average energy differences between GTO and FEM energies in mE_h for C in the unc-aug-cc-pVTZ and AHGBSP3-9 basis sets.

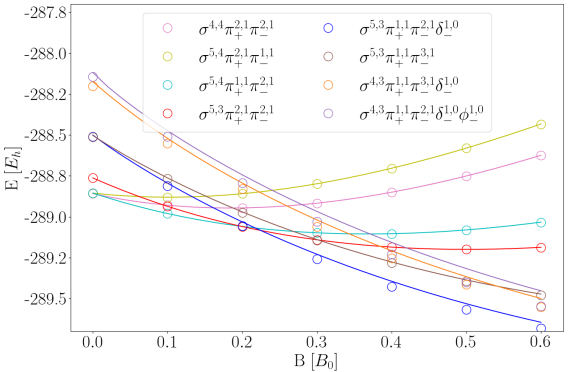
Results

Low lying states of the Si atom in the unc-aug-cc-pVTZ basis set.



Results

Low lying states of the Si atom in the AHGBSP3-9 basis set.



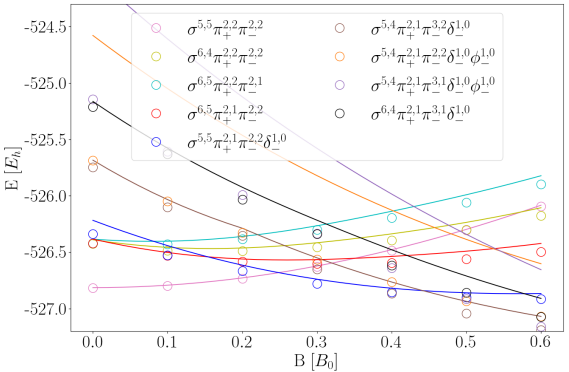
Results

	state	unc-aug-cc-pVTZ	AHGBSP3-9
0	$\sigma^{4,4}\pi_+^{2,1}\pi_-^{2,1}$	4.342	0.085
1	$\sigma^{5,4}\pi_+^{2,1}\pi_-^{1,1}$	4.019	0.203
2	$\sigma^{5,4}\pi_+^{1,1}\pi_-^{2,1}$	4.019	0.203
3	$\sigma^{5,3}\pi_+^{2,1}\pi_-^{2,1}$	4.743	0.186
4	$\sigma^{5,3}\pi_+^{1,1}\pi_-^{2,1}\delta_-^{1,0}$	43.846	26.202
5	$\sigma^{5,3}\pi_+^{1,1}\pi_-^{3,1}$	23.209	6.468
6	$\sigma^{4,3}\pi_+^{1,1}\pi_-^{3,1}\delta_-^{1,0}$	74.118	40.056
7	$\sigma^{4,3}\pi_+^{1,1}\pi_-^{2,1}\delta_-^{1,0}\phi_-^{1,0}$	157.267	61.168

Mean average energy differences between GTO and FEM energies in mE_h for Si in the unc-aug-cc-pVTZ and AHGBSP3-9 basis sets.

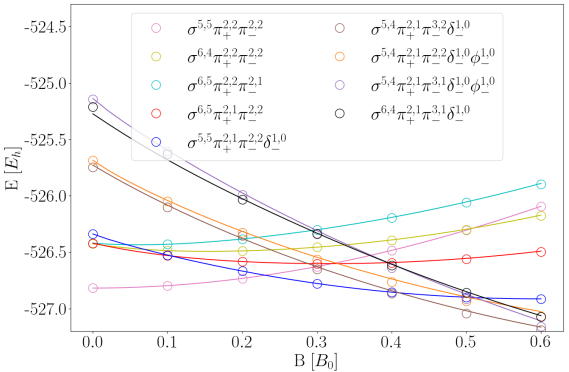
Results

Low lying states of the Ar atom in the unc-aug-cc-pVTZ basis set.



Results

Low lying states of the Ar atom in the AHGBSP3-9 basis set.

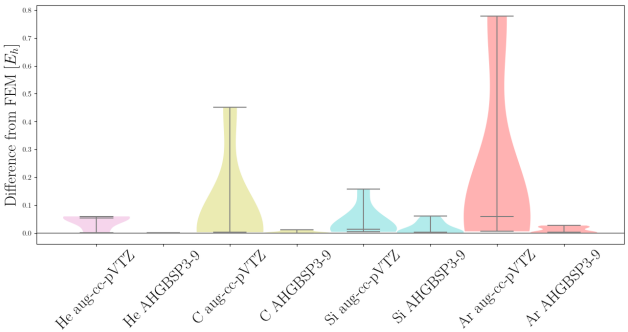


Results

	state	unc-aug-cc-pVTZ	AHGBSP3-9
0	$\sigma^{5,5}\pi_+^{2,2}\pi_-^{2,2}$	5.710	0.016
1	$\sigma^{6,4}\pi_+^{2,2}\pi_-^{2,2}$	46.060	1.752
2	$\sigma^{6,5}\pi_+^{2,2}\pi_-^{2,1}$	45.779	2.119
3	$\sigma^{6,5}\pi_+^{2,1}\pi_-^{2,2}$	45.779	2.119
4	$\sigma^{5,5}\pi_+^{2,1}\pi_-^{2,2}\delta_-^{1,0}$	59.510	0.062
5	$\sigma^{5,4}\pi_+^{2,1}\pi_-^{3,2}\delta_-^{1,0}$	88.711	21.867
6	$\sigma^{5,4}\pi_+^{2,1}\pi_-^{2,2}\delta_-^{1,0}\phi_-^{1,0}$	765.591	20.442
7	$\sigma^{5,4}\pi_+^{2,1}\pi_-^{3,1}\delta_-^{1,0}\phi_-^{1,0}$	779.603	26.642
8	$\sigma^{6,4}\pi_+^{2,1}\pi_-^{3,1}\delta_-^{1,0}$	111.424	22.786

Mean average energy differences between GTO and FEM energies in mE_h for Ar in the unc-aug-cc-pVTZ and AHGBSP3-9 basis sets.

Conclusions



- ✓ Interesting chemistry
- ✓ Standard GTO basis sets fall short
- ✓ It is possible to capture the effects with GTOs

Future work

- Use these results to tailor GTO basis sets for intermediate magnetic field applications
- Implement complex orbitals to the atomic GTO calculations

Acknowledgements

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