Electronic excitations in cyanines with state-of-the-art multireference methods

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This is the abstract

Keywords: cyanine; excited states; multireference methods

I. INTRODUCTION

Unless otherwise stated, atomic units are used throughout.

II. COMPUTATIONAL DETAILS

III. CONCLUSION

ACKNOWLEDGMENTS

This work was performed using HPC resources from CALMIP (Toulouse) under allocation 2016-0510 and from GENCI-TGCC (Grant 2016-08s015).

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TABLE I. Ground-state energy of cyanines for various methods and basis sets.

Method	Basis	Ground-state energy of cyanines				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE II. Excited-state energy of cyanines for various methods and basis sets.

Method	Basis	Excited-state energy of cyanines				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE III. Vertical excitation energy of cyanines (in eV) for various methods and basis sets.

Method	Basis	Vertical excitation energy of cyanines (in eV)				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE IV. Ground-state DMC energy of cyanines for various trial wave functions. The statistical error is reported in parenthesis.

Trial wave function	Basis	Ground-state DMC energy of cyanines				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE V. Excited-state DMC energy of cyanines for various trial wave functions. The statistical error is reported in parenthesis.

Trial wave function	Basis	Excited-state DMC energy of cyanines				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE VI. Vertical excitation DMC energy of cyanines (in eV) for various trial wave functions. The statistical error is reported in parenthesis.

Trial wave function	Basis	Vertical excitation DMC energy of cyanines (in eV)				
		C3	C5	C7	C9	C11
HF	AVDZ					
	AVTZ					
	AVQZ					
CISD	AVDZ					
	AVTZ					
	AVQZ					
CAS	AVDZ					
	AVTZ					
	AVQZ					
$(SC)^2$-CI	AVDZ					
	AVTZ					
	AVQZ					
DD-CI	AVDZ					
	AVTZ					
	AVQZ					
MR-CISD	AVDZ					
	AVTZ					
	AVQZ					
DD-CC	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD	AVDZ					
	AVTZ					
	AVQZ					
MR-CCSD(T)	AVDZ					
	AVTZ					
	AVQZ					
FCI/CIPSI	AVDZ					
	AVTZ					
	AVQZ					

TABLE VII. Comparison of vertical excitation energy of cyanines (in eV) for various methods.

Method	Vertical excitation energy of cyanines (in eV)					
	C3	C5	C7	C9	C11	
Wave function methods						
CISD						This work
CAS						This work
$(SC)^2$-CI						This work
DD-CI						This work
MR-CISD						This work
DD-CC						This work
MR-CCSD						This work
MR-CCSD(T)						This work
FCI/CIPSI						This work
DMC calculations						
CISD						This work
CAS						This work
$(SC)^2$-CI						This work
DD-CI						This work
MR-CISD						This work
DD-CC						This work
MR-CCSD						This work
MR-CCSD(T)						This work
FCI/CIPSI						This work
Reference calculations						
exCC3	7.16	4.84	3.65	2.96	2.53	Ref. 1
DMC	7.38(2)	5.03(2)	3.83(2)	3.09(2)	2.62(2)	Ref. 1
CASPT2	7.19	4.69	3.53	2.81	2.46	Ref. 1
GW/BSE		4.80	3.63	2.96	2.48	Ref. 2
TD-DFT calculations						
TD-PBE	7.40	5.22	4.11	3.44	2.98	Ref. 1
TD-PBE0	7.62	5.33	4.18	3.50	3.03	Ref. 1
TD-B2PLYP	7.30	5.05	3.92	3.25	2.80	Ref. 1
TD-CAM-B3LYP	7.55	5.26	4.12	3.44	2.97	Ref. 1
TD-MO6-2X		5.23	4.09	3.41	2.95	Ref. 3