Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

A RASSCF study of free base, magnesium and zinc porphyrins: accuracy versus efficiency

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Electronic Supplementary Information

Tables

State	a_u	b_{1u}	b_{2g}	b_{3g}	Weight (%)
$1\ ^1A_g$	2 0	2 2 2 0	2 2 0 0	2 2 0 0	80.9
$1\ ^1B_{2u}$	d 0	2 2 2 0	2 2 u 0	2 2 0 0	46.0
	2 0	2 2 u 0	2 2 0 0	2 2 d 0	33.5
$1\ ^1B_{3u}$	2 0	2 2 u 0	2 2 d 0	2 2 0 0	42.0
	d 0	2 2 2 0	2 2 0 0	2 2 u 0	30.5
$2\ ^1B_{2u}$	2 0	2 u 2 0	2 2 0 0	2 2 d 0	30.6
	2 0	2 2 u 0	2 2 0 0	2 2 d 0	21.4
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	10.9
$2\ ^1B_{3u}$	2 0	2 u 2 0	2 2 d 0	2 2 0 0	41.4
	d 0	2 2 2 0	2 2 0 0	2 2 u 0	14.8
$3\ ^1B_{2u}$	2 0	2 2 u 0	2 2 0 0	2 2 d 0	21.5
	2 0	2 u 2 0	2 2 0 0	2 2 d 0	20.1
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	19.5
$3\ ^1B_{3u}$	d 0	2 2 2 0	2 2 0 0	2 2 u 0	24.2
	2 0	2 2 u 0	2 2 d 0	2 2 0 0	19.9
	2 0	2 u 2 0	2 2 d 0	2 2 0 0	14.6
$4\ ^1B_{2u}$	2 0	u 2 2 0	2 2 0 0	2 2 d 0	63.1
	d 0	2 2 2 0	2 u 0 0	2 2 2 0	10.0
$4\ ^1B_{3u}$	2 0	u 2 2 0	2 2 d 0	2 2 0 0	40.5
	d 0	2 2 2 0	2 u d 0	2 2 u 0	10.7

Table S1. Occupations of active space orbitals in leading configurations the ^1A_g ground and low lying $^1B_{2u}$ and $^1B_{2u}$ excited states of free base porphyrin. Only those configurations with weight greater than 10% are shown. 2 = doubly occupied, u = singly occupied (spin up), d = single occupied (spin down), 0 = unoccupied.

Active Space	CSFs (%)
CASSCF(16,14)	537,705 (100)
RASSCF(16,2,2;8,0,6)	325 (0.06)
RASSCF(16,3,3;8,0,6)	3,545 (0.66)
RASSCF(16,4,4;8,0,6)	22,685 (4.22)
RASSCF(16,2,2;6,4,4)	4,628 (0.86)
RASSCF(16,3,3;6,4,4)	33,448 (6.22)
RASSCF(16,4,4;6,4,4)	127,911 (23.79)
RASSCF(16,3,3;5,5,4)	57,683 (10.72)
RASSCF(16,3,3;4,6,4)	80,665 (15.00)
RASSCF(16,3,3;3,7,4)	96,756 (17.99)
RASSCF(16,4,4;3,7,4)	250,171 (46.53)
RASSCF(16,5,5;3,7,4)	412,215 (76.77)
RASSCF(16,3,3;2,8,4)	103,936 (19.33)
RASSCF(16,4,4;2,8,4)	254,685 (47.37)
RASSCF(26,2,2;13,0,11)	2,665 (0.49)
RASSCF(26,3,3;13,0,11)	94,500 (17.57)
RASSCF(26,2,2;11,4,9)	63,258 (11.76)
RASSCF(26,3,3;11,4,9)	1,877,565 (349.18)

Table S2. Number of configuration state functions (CSFs) in the CI-space for varying levels of MCSCF calculations on ground states of H_2P, MgP and ZnP. Details of the active space compositions are given in the main text. Percentage values are relative to the CASSCF(16,14) reference.

State	a_u	b_{1u}	b_{2g}	b_{3g}	Weight (%)
$1\ ^1A_g$	0 0	2 2 2 0	2 2 0 0	2 2 0 0	82.0 (82.2)
$1\ ^1E_u$ ($^1B_{2u}$)	2 0	2 2 u 0	2 2 0 0	2 2 d 0	38.5 (37.6)
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	38.0 (38.7)
$1\ ^1E_u$ ($^1B_{3u}$)	2 0	2 2 u 0	2 2 d 0	2 2 0 0	38.5 (37.6)
	d 0	2 2 2 0	2 2 2 0	2 2 u 0	38.0 (38.7)
$2\ ^1E_u$ ($^1B_{2u}$)	2 0	2 u 2 0	2 2 0 0	2 2 d 0	42.9 (44.6)
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	13.1 (11.7)
	2 0	2 2 u 0	2 2 0 0	2 2 d 0	12.1 (11.5)
$2\ ^1E_u$ ($^1B_{3u}$)	2 0	2 u 2 0	2 2 d 0	2 2 0 0	42.9 (44.6)
	d 0	2 2 2 0	2 2 0 0	2 2 u 0	13.1 (11.7)
	2 0	2 2 u 0	2 2 d 0	2 2 0 0	12.1 (11.5)
$3\ ^1E_u$ ($^1B_{2u}$)	2 0	u 2 2 0	2 2 0 0	2 2 d 0	20.1 (19.4)
	2 0	2 u 2 0	2 2 0 0	2 2 d 0	17.8 (15.3)
	2 0	2 2 u 0	2 2 0 0	2 2 d 0	15.8 (18.0)
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	13.9 (15.7)
$3\ ^1E_u$ ($^1B_{3u}$)	2 0	u 2 2 0	2 2 d 0	2 2 0 0	20.1 (19.4)
	2 0	2 u 2 0	2 2 d 0	2 2 0 0	17.8 (15.3)
	2 0	2 2 u 0	2 2 d 0	2 2 0 0	15.8 (18.0)
	d 0	2 2 2 0	2 2 0 0	2 2 u 0	13.9 (15.7)
$4\ ^1E_u$ ($^1B_{2u}$)	2 0	u 2 2 0	2 2 0 0	2 2 d 0	27.3 (28.3)
	d 0	2 2 2 0	2 2 u 0	2 u d 0	13.1 (13.8)
	d 0	2 2 2 0	2 2 u 0	2 2 0 0	10.7 (9.6)
$4\ ^1E_u$ ($^1B_{3u}$)	2 0	u 2 2 0	2 2 d 0	2 2 0 0	27.3 (28.3)
	d 0	2 2 2 0	2 u d 0	2 2 u 0	13.1 (13.8)
	d 0	2 2 2 0	2 2 0 0	2 2 u 0	10.7 (9.6)

Table S3. Occupations of active space orbitals in leading configurations the ^1A_g ground and low lying ^1E_u excited states of magnesium and zinc porphyrin. Only those configurations with weight greater than 10% are shown. 2 = doubly occupied, u = singly occupied (spin up), d = single occupied (spin down), 0 = unoccupied.

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Figure Captions

Figure S1. Comparison of the natural occupation numbers of the frontier orbitals of MgP and ZnP calculated using different active spaces. Solid circles correspond to integer occupancies of 0, 1 and 2 whilst dashed circles indicate occupancies of 0.1, 0.9, 1.1 and 1.9. Occupations lying between the values marked by the dashed circles indicate strongly multiconfigurational character[63].

Figure S2. Density differences of excited states of MgP and ZnP, calculated using different active spaces approaches. (a) CASSCF(16,14)-RASSCF(16,3,3;6,4,4) (b) CASSCF(16,14)-RASSCF(16,3,3;2,8,4).