STUDY OF BASIS SET CONVERGENCE

The study of convergence of the Sr and interstice basis sets has been done at the minimal RAS($4f/5d6s$-$1e$) level possible to obtain electronic excited states of the $4f^{13}5d(e_g)$, $4f^{13}5d(t_{2g})$, and $4f^{13}[6s/\phi_{ITE}](a_{1g})$ manifolds of Yb^{2+}, in addition to the ground states of Yb^{2+} and Yb^{3+}-doped $SrCl_2$. The choice of this simple RAS is justified by the observed independence of basis set effects and RAS definition observed in Table IV and discussed in Sec. III B of the paper. The results of the study are presented in Table I and Fig. 1 of this document. The steps followed and conclusions driven from this study are commented and listed next referring to sections A to F of Table I.

A) As expected, the frozen $4s$ and $4p$ orbitals of the Sr^{2+} embedded ion are very important as shown by the results of the Sr$[1s, 1p]$ basis set. The bond lengths increase by 0.06 – 0.1 Å and the effects on the adiabatic transition energies, T_e, are significant, and large, in the IP (upper graphs of Fig. 1).

B) and C) bases reveal that, although the contracted $5s$ and $5p$ orbitals obtained in Sr^+-embedded ion calculations do not affect the results, the GTF released in their splittings up to quadruple-zeta (QZ) lead to reasonably converged properties, as shown by the Sr$[5s, 1p]$ (B) and Sr$[5s, 5p]$ results (C), respectively. The $5s$ and $5p$ embedded ion orbitals have the nodal structure corresponding to a Sr^+ embedded ion. The cluster wavefunctions studied do not seem to need it; rather, they make use of the free GTF spanning their more external lobes. (cf. upper graphs of Fig. 1)

D) Given their negligible effect, the contracted $5s$ and $5p$ orbitals are removed from basis set Sr$[5s, 5p]$ of C. After removal, the Sr$[4s, 4p]$ results show no loss of accuracy. Hence, this converged basis set suggests a recipe for constructing first neighbour cations basis sets as follows: The outermost, frozen embedded ion orbitals must be used (to fulfil cluster-embedding orthogonality) together with the GTF with significant coefficients in the outer lobes of the empty cation orbitals, forming, altogether, at least a QZ basis set.

E) Given that the ANO-RCC basis sets are used for Yb and Cl in the defect cluster, the Sr $4s$ and $4p$ embedded ion orthogonalization functions are combined with 4 s-type and 3 p-type GTF of the ANO-RCC Sr basis set, which satisfy the recipe derived in D: those with largest contribution to the $5s$ and $5p$ atomic natural orbitals of Sr. The results are very close to those of the embedded ion basis set, shown in D.

F) Finally, basis set Sr[$5s$, $4p$] of E is extended locating the 4 s-type primitives of Sr used in basis set E at the (1/2,0,0) interstices of this fluorite-type structure. Their orbital exponents have been scaled by 2^n and n has been optimized so that the energy of the $4f^{13}\phi(a_{1g})$ showing impurity-trapped exciton character at short distance is a minimum. $n = 2$ has turned out to be the optimal value (lower graph of Fig. 1).

Basis set F, consisting of: Yb[$9s8p5d4f3g2h$], Cl[$6s5p3d$], Sr[$5s4p$], and Int[$4s$] functions is considered to be reasonably converged and is used in Table IV C and in Sec. III C.

TABLE I: Effects of extensions to the $(YbCl_8)^{6-}$ cluster and Yb[9*s*8*p*5*d*4*f*3*g*2*h*], Cl[6*s*5*p*3*d*] basis set on properties of the ground state and of representative electronic states of the $4f^{13}5d(e_g)$, $4f^{13}5d(t_{2g})$, and $4f^{13}6s$ manifolds of $SrCl_2$:Yb^{2+}, and on the ground state of $SrCl_2$:Yb^{3+}, calculated at the RASSCF(4*f*) and RASSCF(4*f*/5*d*6*s*-1e) levels. Bond lengths (R_e) are given in Å; totally symmetric vibrational frequencies ($\bar{\nu}_{a_{1g}}$) and adiabatic transitions (T_e) are given in cm^{-1}.

Cluster	basis extension	R_e, $\bar{\nu}_{a_{1g}}$, and T_e [1]								
		$4f^{14}$	$4f^{13}5d(e_g)$	$4f^{13}5d(t_{2g})$				$4f^{13}6s$		$4f^{13}$
		1^1A_{1g}	1^3E_u	2^3E_u	1^3A_{2u}	3^3E_u	1^3A_{1u}	2^3A_{2u} [2]		1^2A_{2u}
$(YbCl_8)^{6-}$	None	2.966	2.930	2.980	2.980	2.979	2.980	3.046		2.804
		204	209	203	202	202	202	193		255
		0	8202	17222	19596	20814	21958	22965	48570	7025
		A) Sr^{2+} 4*s* and 4*p* embedded-ion orbitals for orthogonality								
	Sr[1*s*1*p*]	3.055	3.014	3.069	3.070	3.068	3.069	3.141		2.865
		182	186	182	181	182	181	178		233
		0	9147	16760	19110	20379	21480	20719	59375	15826
$(YbCl_8Sr_{12})^{18+}$		B) A + Sr^{+} 5*s* embedded-ion orbital and its splittings								
	Sr[2*s*1*p*]	3.056	3.015	3.069	3.070	3.068	3.070	3.142		2.865
		182	186	182	181	182	181	178		233
		0	9151	16758	19109	20378	21479	20704	59434	15883
	Sr[3*s*1*p*]	3.056	3.015	3.069	3.071	3.068	3.070	3.142		2.866
		181	186	181	180	181	180	177		232
		0	9132	16687	19032	20301	21398	20588	56781	16172
	Sr[4*s*1*p*]	3.055	3.013	3.069	3.070	3.067	3.069	3.136		2.867
		182	187	183	182	182	181	188		232
		0	8886	16699	19051	20312	21418	20423	52639	16858
	Sr[5*s*1*p*]	3.072	3.027	3.085	3.087	3.084	3.086	3.149		2.877
		178	182	178	177	178	177	198		229
		0	8977	16658	19010	20278	21380	20024	51773	18575
	Sr[6*s*1*p*]	3.077	3.032	3.091	3.092	3.090	3.092	3.153		2.880
		176	181	177	175	176	176	208		228
		0	9035	16641	18990	20262	21362	19882	51314	19155
	Sr[7*s*1*p*]	3.077	3.032	3.091	3.092	3.090	3.092	3.153		2.880
		176	181	177	175	176	175	208		228
		0	9039	16634	18983	20255	21354	19873	51159	19188

C) Sr[5s1p] basis of B + Sr^+ 5p embedded-ion orbital and its splittings

Sr[5s2p]	3.072	3.027	3.085	3.087	3.084	3.087	3.149		2.877
	178	182	178	177	178	177	198		229
	0	8979	16658	19009	20277	21379	20021	51656	18589
Sr[5s4p]	3.096	3.050	3.109	3.111	3.108	3.111	3.178		
	170	176	173	171	172	171	195		
	0	9293	16125	18440	19735	20798	19484	52983	
Sr[5s5p]	3.102	3.056	3.115	3.117	3.114	3.117	3.181		2.892
	170	174	171	169	170	169	201		223
	0	9203	16100	18419	19713	20778	19340	52697	21517
Sr[5s6p]	3.104	3.058	3.117	3.119	3.116	3.119	3.183		2.893
	169	173	170	168	169	168	200		222
	0	9214	16086	18403	19698	20762	19303	52846	21649

D) Sr[5s5p] set of C removing the 5s and 5p CGTF

Sr[4s4p]	3.101	3.056	3.114	3.116	3.113	3.116	3.181		2.892
	170	174	171	169	170	169	200		223
	0	9197	16102	18421	19715	20780	19715	52703	21457

E) Basis set A + 4 s-type and 3 p-type GTF from Yb ANO-RCC basis:
the outermost GTF with significant coefficients in 5s, 5p ANO [3]

Sr[5s4p]	3.101	3.056	3.114	3.116	3.113	3.116	3.180		2.892
	170	174	171	169	171	170	203		223
	0	9263	16113	18429	19724	20785	19333	51777	21454

F) Sr[5s4p] of E + 4 scaled s-type GTF at the 6 (1/2,0,0) Interstices [4]

Int[4s×0.5]	0							48759	
Int[4s×1]	0							47127	
Int[4s×2]	3.101	3.057	3.115	3.117	3.114	3.116	3.180		2.892
	169	173	170	169	171	169	203		223
	0	9114	16058	18378	19670	20736	19260	45824	21461
Int[4s×4]	0							47330	
Int[4s×8]	0							48907	

[1] For each basis set, R_e, $\bar{\nu}_{a_{1g}}$, and T_e are given in the first, second, and third rows, respectively. The energy of 2^3A_{2u} at R(Yb–Cl)= 2.676 Å relative to the minimum of 1^1A_{1g} is also given in the third row.

[2] Crossing between 1 and 2 $^3A_{2u}$ often occurs and causes deformation of 2^3A_{2u} curves.

[3] Orbital exponents: s-type GTF: 0.16177744, 0.07279984, 0.03275992, 0.01474196; p-type GTF: 0.08838988, 0.03977544, 0.01789894.

[4] Values of the optimized scaling factor for the 4 s-type orbital exponents of E.2 are shown.

FIG. 1: Optimization of Sr and Interstice basis sets for the calculation of properties of $SrCl_2$:Yb^{2+}. Upper graphs: Sr basis set dependence of Yb–Cl bond lengths (R_e) and minimum-to-minimum energy differences (T_e) of representative states of the $SrCl_2$:Yb^{2+}. Lower graph: $4s$ Interstice basis set scaling factor optimization. The energy of the excitonic $4f^{13}\phi^{ITE}(a_{1g}) -^3 A_{2u}$ state at R(Yb–Cl) = 2.676Å relative to the $4f^{14} -^1 A_{1g}$ energy minimum is plotted $vs.$ the scaling factor 2^n. All calculations are done at the RAS($4f/5d6s$-$1e$)SCF level. See text for details.

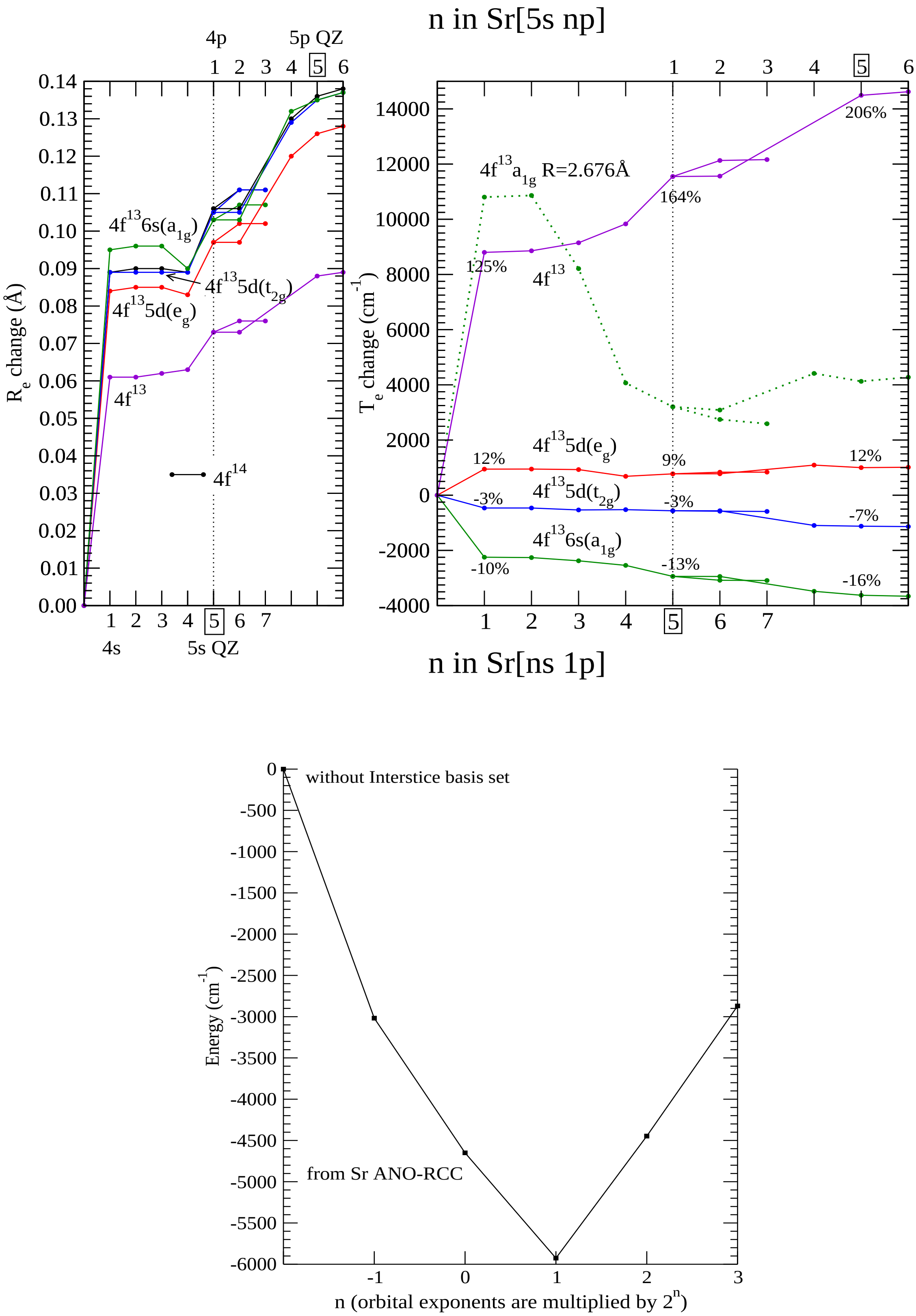
n in Sr[5s np]
4p
5p QZ
R_e change (Å)
4f^13 6s(a_1g)
4f^13 5d(t_2g)
4f^13 5d(e_g)
4f^13
4f^14
4s
5s QZ
T_e change (cm^-1)
4f^13 a_1g R=2.676Å
125%
164%
206%
12%
9%
-3%
-7%
-10%
-13%
-16%
n in Sr[ns 1p]
without Interstice basis set
from Sr ANO-RCC
Energy (cm^-1)
n (orbital exponents are multiplied by 2^n)

Figure 1.