Supplementary material for: Accurate many-body electronic structure near the basis set limit: application to the chromium dimer

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ENERGY CONVERGENCE IN AHLRICHS SV BASIS

For Cr_2, the Ahlrichs SV basis [1] (somewhat confusingly named Ahlrichs VDZ basis at the Basis Set Exchange [2]) is too small to give even a qualitatively correct potential energy curve [3]. The predicted equilibrium bond length is much too long. However, Cr_2 at a bond length of 1.5 Å in this basis has become a very popular system for testing the accuracy and efficiency of electronic structure methods [3–14]. Since the SHCI method has progressed considerably after publishing our earlier calculations for this basis, we provide updated information here.

Table I and Figs. 1 and 2 show the convergence of the energy, for both frozen Mg-core calculations (excitation space of $(24e, 30o)$), and for all electron excitation calculations (excitation space of $(48e, 42o)$). The (24e,30o) energies depend on the nature of the frozen core orbitals. We studied freezing Hartree-Fock (HF) core orbitals and freezing core natural orbitals from a CAS(12e,12o) space. To get the energy extrapolated to $\epsilon_1 = 0$, rather than fitting to a polynomial in ϵ_1, it is preferable [15] to fit to a polynomial in $E_{\rm var} - E_{\rm tot}$. In Figs. 1 and 2 the solid lines are weighted quartic fits, using $1/(E_{\rm var} - E_{\rm tot})^2$ as the weight function. In some curves a spline fit is used for part of the range, but these coincide with the quartic fits within the thickness of the lines over almost all the range. We also show linear fits (dashed lines) using just the 4 points with ϵ_1 ranging from 2×10^{-5} to 2×10^{-4} Ha (the largest 4 values of ϵ_1 shown in the plots) merely to demonstrate the error resulting from not going to sufficiently small values of ϵ_1 (sufficiently large $N_{\rm det}$). From the figures, it is apparent that the weighted quartic fits provide more accurate extrapolated energies. The quartic fits are possible only because we went down to sufficiently small values of ϵ_1 and because the statistical uncertainties in our calculations are very small, particularly for the smaller ϵ_1 values. The Table shows that the iCIPT2 energies in a very recent preprint [14] agree very well with our linear extrapolations, but not as well with the more accurate weighted quartic extrapolation. The extrapolated energies in Table I for HF-core $(24e, 30o)$, CAS-core $(24e, 30o)$ and $(48e, 42o)$ should be accurate to 0.005, 0.005 and 0.01 mHa respectively and should serve as a reference for other methods. In case the reader is surprised that the weighted quartic fits for $E_{\rm var}$ and $E_{\rm tot}$ extrapolate to precisely the same point, we note that the expansion coefficients for the two fits are precisely the same, except that the linear coefficients differ by 1.

The convergence of the energies versus the number of determinants can be improved by using orbitals with L_z rather than d2h point group symmetry, and by optimizing the orbitals [16]. This is the reason why in Table I, for a given value of $N_{\rm det}$, the energies in the first block are better converged than those in the second block, each relative to its converged value. Besides these two changes, there is yet another improvement that can be made to the convergence of the (48e,42o) calculations. The usual SHCI selection criterion in Eq. 2 of the main paper does not take into account the large differences in the energy denominator of 2^{nd}-order perturbation theory when core excitations are allowed. An efficient way to remove unimportant high excitation energy determinants is to add a second selection criterion,

$$\frac{(H_{ai}c_i)^2}{\max\left(\sum_i e_{a,i} - \sum_i e_{{\rm HF},i}, 0\right)} > c\epsilon^2, \tag{1}$$

where $e_{{\rm HF},i}$ and $e_{a,i}$ are the 1-body energies of the i^{th} occupied orbital in the HF determinant and in determinant D_a respectively. If $c = 0$, the additional selection criterion has no effect. We used $c = 0.2$. The resulting improvement in the convergence is shown in Fig. 3. For this system, SHCI with L_z optimized orbitals and the additional selection criterion converges slightly faster than iCIPT2 [14], but more importantly SHCI can go to much larger $N_{\rm det}$.

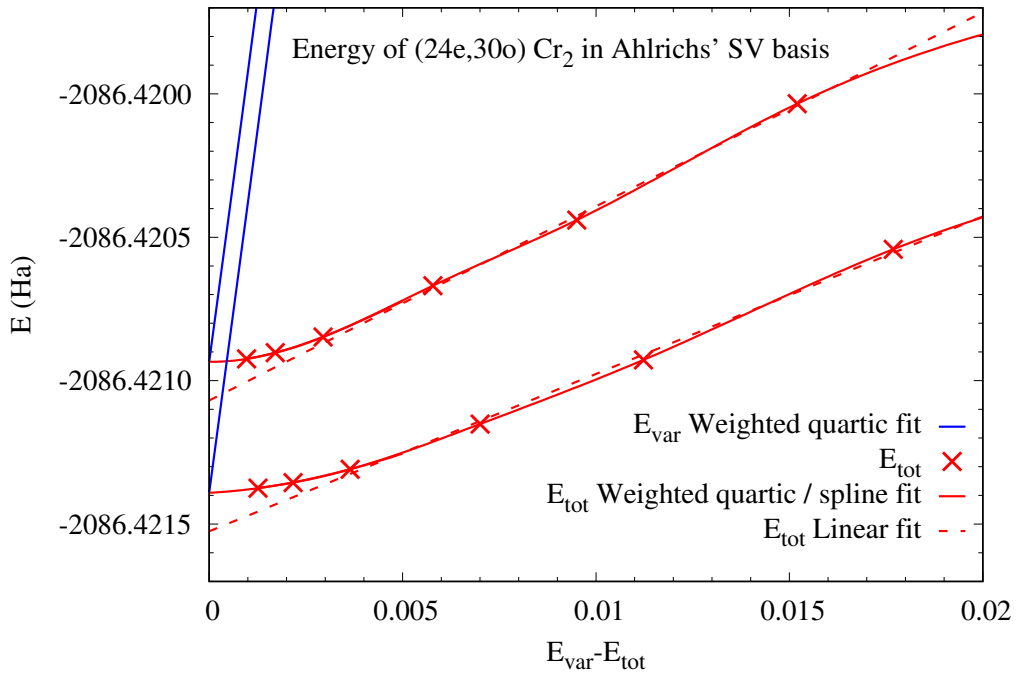

FIG. 1. Convergence of the frozen Mg-core (24e,30o) total and variational energies. The upper pair of curves freeze the core in HF orbitals and the lower pair in CAS(12,12) natural orbitals.

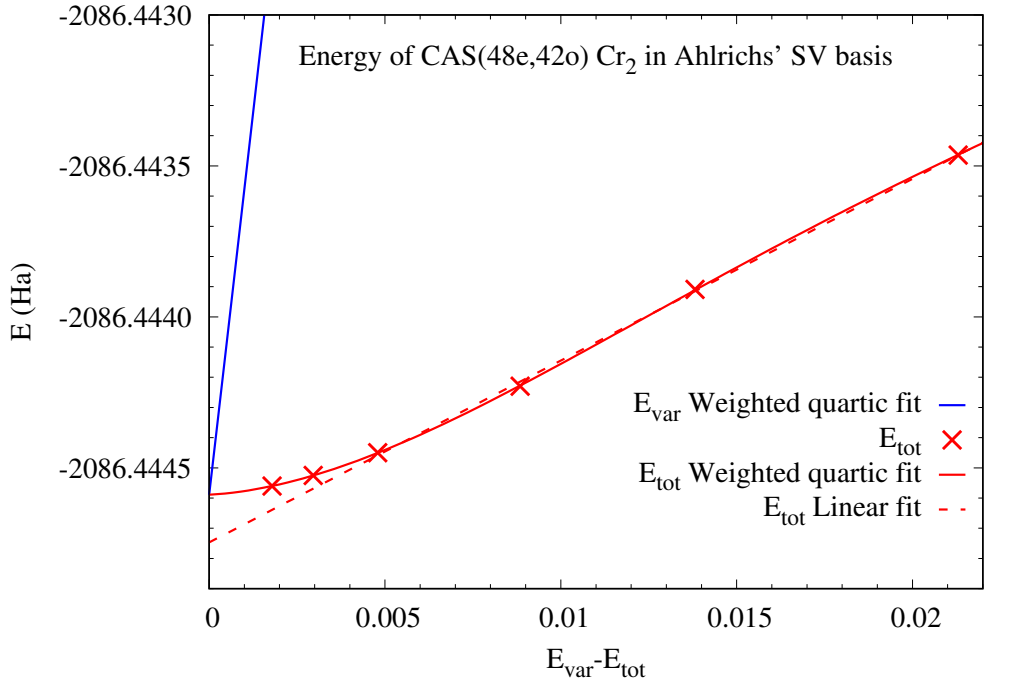

FIG. 2. Convergence of the all-electron (48e,42o) total and variational energies.

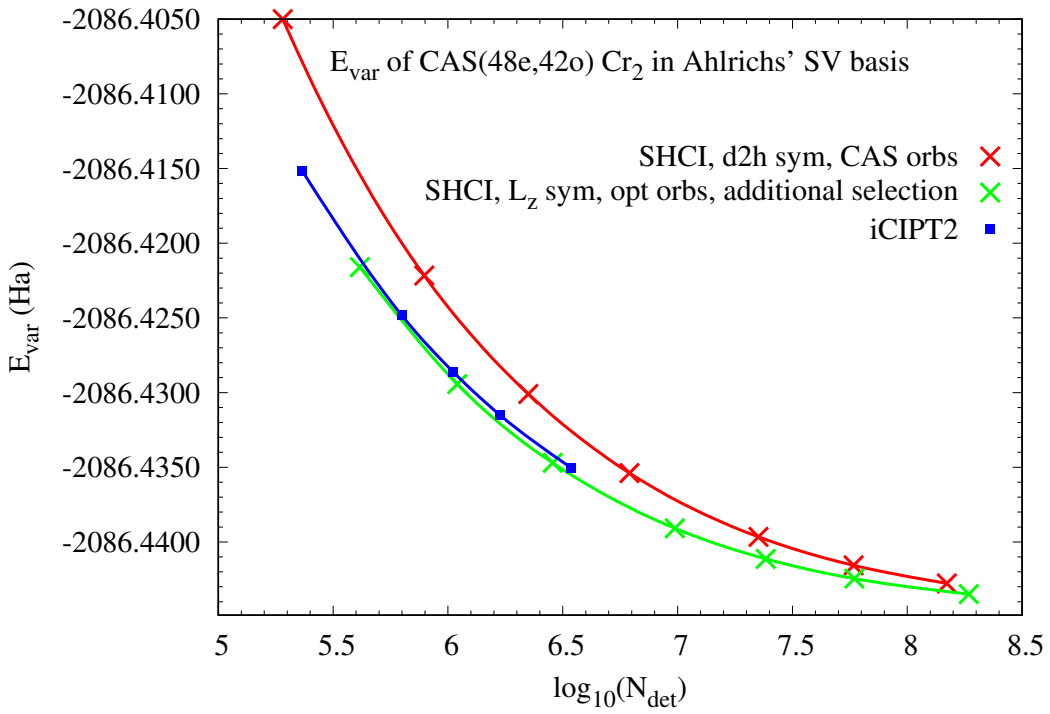

FIG. 3. Demonstration of improvement in convergence of the (48e,42o) variational energy upon using L_z symmetry, optimized orbitals and the additional selection criterion. The iCIPT2 energies of Ref. 14 are also shown.

We end by noting that the energy of course depends on the choice of which orbitals are frozen (HF orbitals or CAS natural orbs) because this changes the active space in which the calculation is done. This makes a difference of 0.45 mHa to the converged energy as can be seen in Fig. 1 and Table 1. On the other hand, once the core orbitals are selected, the choice of which orbitals to use in the active space (d2h or Lz symmetry, and, natural orbitals or optimized orbitals), and whether we use the second selection criterion or not, affects only the rate of convergence; the final converged energy is unchanged to within the stated accuracy of 0.005, 0.005 and 0.01 mHa.

TABLE I. Convergence of Cr_2 variational and total energies at r=1.5 Å, in the (24e,30o) and (48e,42o) spaces using the Ahlrichs SV basis versus ϵ_1 (see Eq. 2 and surrounding text of the main paper). The energy in the (24e,30o) space is 0.46 mHa deeper if the frozen core orbitals are CAS(12,12) natural orbitals rather than Hartree-Fock (HF) orbitals. Most papers in the literature appear to use the CAS(12,12) core, but some papers do not specify. $N_{\rm det}$ is the number of determinants in the variational wavefunction. The estimated statistical and/or extrapolation errors in the last digit(s) of $E_{\rm tot}$ are in parentheses. The most accurate extrapolation is shown in bold face. In both spaces, the iCIPT2 [14] energies agree very well with the linear extrapolations, but less well with the more accurate weighted quadratic extrapolations. The timings shown are for 2 Intel Xeon E5-2620 v4 nodes, each with 16 physical cores running at 2.1 Gz.

		Energy + 2086 (Ha)		Real time (sec)	
ϵ_1 (Ha)	$N_{\rm det}$	$E_{\rm var}$	$E_{\rm tot}$	var	PT2
		Excit. space (24e,30o)			
		Hartree-Fock core			
		Optimized L_z orbitals			
5×10^{-4}	113 322	-0.390 528	-0.419 564(10)	1	37
2×10^{-4}	429 970	-0.404 833	-0.420 035(8)	5	53
1×10^{-4}	1 108 805	-0.410 938	-0.420 440(6)	11	76
5×10^{-5}	2 854 759	-0.414 887	-0.420 669(4)	36	128
2×10^{-5}	9 505 470	-0.417 904	-0.420 848(1)	183	416
1×10^{-5}	23 037 614	-0.419 193	-0.420 903(1)	541	866
5×10^{-6}	54 367 230	-0.419 958	-0.420 924(0)	1625	1346
0 [a]			**-0.420 934(5)**		
0 [b]			-0.421 07		
		Excit. space (24e,30o)			
		CAS(12e,12o) core			
		CAS d2h orbitals			
5×10^{-4}	123 144	-0.387 661	-0.420 094(10)	1	37
2×10^{-4}	480 138	-0.402 856	-0.420 541(7)	5	64
1×10^{-4}	1 276 421	-0.409 702	-0.420 927(6)	14	100
5×10^{-5}	3 306 031	-0.414 146	-0.421 151(4)	45	176
2×10^{-5}	11 254 965	-0.417 662	-0.421 308(1)	243	537
1×10^{-5}	27 694 681	-0.419 185	-0.421 355(1)	698	1254
5×10^{-6}	66 679 956	-0.420 114	-0.421 375(1)	2288	1848
0 [a]			**-0.421 385(5)**		
0 [b]			-0.421 52		
iCIPT2 [14]	CAS core	-0.416 130	-0.421 470(16)		
ASCI [10]	unknown core	-0.403 88	-0.420 3		
ASCI [13]	unknown core		-0.420 517		
DMRG [9]	HF core	-0.420 78	-0.420 948(34)		
FCIQMC [5]	HF core		-0.421 2(3)		
DMRG [4]	unknown core	-0.420 82	-0.421 00		
DMRG [3]	HF core	-0.420 525	-0.421 156		
CCSDTQ [9]	HF core		-0.406 696		
		Excit. space (48e,42o)			
		CAS d2h orbitals			
5×10^{-4}	190 937	-0.405 001	-0.442 899(10)	3	278
2×10^{-4}	787 919	-0.422 163	-0.443 463(7)	13	293
1×10^{-4}	2 237 828	-0.430 093	-0.443 908(4)	40	569
5×10^{-5}	6 171 642	-0.435 388	-0.444 229(4)	145	1091
2×10^{-5}	22 484 929	-0.439 657	-0.444 450(1)	846	2177
1×10^{-5}	58 390 489	-0.441 566	-0.444 525(1)	2671	2631
5×10^{-6}	148 589 206	-0.442 773	-0.444 560(1)	10981	2994
0 [a]			**-0.444 586(10)**		
0 [b]			-0.444 75		
iCIPT2 [14]		-0.435 048	-0.444 740(41)		
ASCI [10]			-0.443 25		
DMRG [9]		-0.443 334	-0.444 78(32)		
CCSDTQ [9]			-0.430 244		

[a] Weighted quartic fit

[b] Linear fit to 4 points with ϵ_1 ranging from 2×10^{-5} to 2×10^{-4} Ha.

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