

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

Junhao Li,¹ Yuan Yao,¹ Adam A. Holmes,^{1,2} Matthew Otten,¹ Qiming Sun,^{3,4} Sandeep Sharma,² and C. J. Umrigar¹

¹Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853, USA

²Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, CO 80302, USA

³Tencent America LLC, Palo Alto, CA 94036, USA

⁴Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

We describe a method for computing near-exact energies for correlated systems with large Hilbert spaces. The method efficiently identifies the most important basis states (Slater determinants) and performs a variational calculation in the subspace spanned by these determinants. A semistochastic approach is then used to add a perturbative correction to the variational energy to compute the total energy. The size of the variational space is progressively increased until the total energy converges to within the desired tolerance. We demonstrate the power of the method by computing a near-exact potential energy curve (PEC) for a very challenging molecule – the chromium dimer.

Introduction: The evaluation of accurate energies for correlated many-electron systems is one of the most important challenges for computational science. The difficulty arises from the fact that the number of many-electron states increases combinatorially with the number of single-electron states (orbitals) N_{orb} and the number of up- and down-spin electrons, N_{\uparrow} , N_{\downarrow} ($N = N_{\uparrow} + N_{\downarrow}$) as $N_{\text{orb}}^{N_{\uparrow}} C_{N_{\uparrow}} \times N_{\text{orb}}^{N_{\downarrow}} C_{N_{\downarrow}}$.

There exist a number of accurate methods for weakly correlated systems, which we define for the purpose of this paper as systems for which much of the wavefunction amplitude resides on a relatively small number of many-electron basis functions (Slater determinants), all of which can be constructed by exciting electrons from the orbitals of a reference state to orbitals within a small set of “active” orbitals.¹ In that case it is possible to perform an exact diagonalization in the complete active space (CAS), i.e. space spanned by all determinants reachable by any number of excitations among these active orbitals. If the orbitals are rotated to optimize the energy, the resulting method is called the complete active space self-consistent field (CASSCF) method^{2,3}. The resulting energy can be improved by performing second-order perturbation theory to approximately include the contribution of additional states, resulting in the complete active space perturbation theory (CASPT2) method⁴.

At the other end of the spectrum, very strongly correlated systems can be defined as those systems for which it is necessary to include a large fraction of all possible Slater determinants to get an accurate energy and other expectation values. For these systems there is no recourse other than exact diagonalization in the entire Hilbert space, which is feasible only for very small systems or very small basis sets.

In between these two extremes, moderately strongly correlated systems require a large number of important

Slater determinants to obtain accurate results, but this number constitutes a vanishingly small fraction of the dimension of the Hilbert space. Further, these states do not have any obvious pattern (e.g. they do not all belong to a CAS space). Many *ab initio* Hamiltonians belong to this category. It is for these systems that selected configuration interaction plus perturbation theory (SCI+PT), first developed about 50 years ago^{5,6}, can be most useful. Recently there has been renewed interest in these methods^{7–15} and some interesting applications, particularly to excited states^{14,16}. The recent development of a very efficient algorithm in the form of the semistochastic heat-bath configuration interaction (SHCI) method by some of the authors of this paper^{17–21} has now made it possible to perform calculations on a wider and more interesting set of systems. We next briefly describe the SHCI method and the main innovations that account for its efficiency. Then we apply the SHCI method to calculate the potential energy curve of a small but very challenging molecular system, the chromium dimer.

Method: Selected configuration interaction plus perturbation theory (SCI+PT) methods approximate the full configuration interaction (FCI) energy by selecting the most important determinants from a large Hilbert space. These methods contain two steps. In the first step a set of important determinants, \mathcal{V} , are selected and the Hamiltonian is diagonalized in the subspace of these determinants to obtain the lowest, or the lowest few, eigenstates. In the second step, a second-order perturbation theory is used to calculate the energy contributions of the determinants that are in a space \mathcal{P} that is disjoint to \mathcal{V} , but that have a non-zero Hamiltonian matrix element connecting them to at least one of the determinants in \mathcal{V} . We will refer to \mathcal{V} and \mathcal{P} as the variational and perturbative spaces, respectively. The recently developed SHCI algorithm substantially reduces the computational time of performing both the variational calculation and the perturbative correction, and eliminates the memory

bottleneck for the perturbative calculation. We describe these two innovations next.

The method used in this paper is an improved version of the one recently developed²¹ by some of the authors of this paper. Straightforward SCI+PT implementations use an energetic criterion based on 2^{nd} -order perturbation theory,

$$\frac{(\sum_{D_i \in \mathcal{V}} H_{ai} c_i)^2}{E - E_a} < -\epsilon, \quad (1)$$

for selecting determinants, D_a , to be included in \mathcal{V} . In Eq. 1, E is the energy of the variational wavefunction and E_a is the energy of determinant D_a . SHCI modifies the selection criterion to

$$\max_{D_i \in \mathcal{V}} |H_{ai} c_i| > \epsilon_1, \quad (2)$$

which greatly reduces the cost by taking advantage of the fact that most of the H_{ai} matrix elements are 2-body excitations, which depend only on the indices of the 4 orbitals whose occupations change and not on the other occupied orbitals of a determinant¹⁷. Thus by sorting the absolute values of all possible matrix elements of the 2-body excitations in descending order prior to the start of the SHCI selection algorithm, the scan over determinants D_a can be terminated as soon as $|H_{ai}|$ drops below $\epsilon_1/|c_i|$. In this paper, a similar idea is used to speed up the selection of 1-body excitations as well. This enables a procedure in which *only the important determinants are ever looked at*, resulting in orders of magnitude saving in computer time. SHCI uses an analogous procedure to also efficiently select the important perturbative determinants in \mathcal{P} , replacing the variational cutoff ϵ_1 in Eq. (2) with a much smaller perturbative cutoff $\epsilon_2 \ll \epsilon_1$.

Even with this improvement, a straightforward evaluation of the perturbative correction has a very large memory requirement because all distinct determinants in \mathcal{P} that meet the criterion in Eq. 2 with ϵ_1 replaced by ϵ_2 must be stored.²² For the systems in this paper, the total number of connected determinants is $> 10^{15}$ ($> 10^{13}$ *distinct* connected determinants) when the number of variational determinants is on the order of 10^9 . To solve this problem, we have developed a 2-step¹⁸, and later an improved 3-step²¹ semistochastic perturbative approach that overcomes this memory bottleneck, and is fast and perfectly parallelizable. A different efficient semistochastic perturbative approach has been used in Ref. 11. These improvements allowed us to use 2×10^9 variational determinants²¹, which is two orders of magnitude larger than the largest variational space of 2×10^7 determinants¹¹ used in any other SCI+PT method.

We choose $\epsilon_2 = 10^{-6} \epsilon_1$, so by progressively reducing the single parameter ϵ_1 a systematic convergence to the full configuration interaction limit is obtained. The energy at the $\epsilon_1 = 0$ limit is obtained using a quadratic

fit to the energies versus the perturbative correction¹⁹. The convergence of the energy depends greatly on the choice of orbitals. Natural orbitals give faster convergence than Hartree Fock orbitals. Orbitals that are optimized to minimize the SHCI energy²⁰ for a large value of ϵ_1 yield yet faster convergence, but the optimization typically requires many more optimization iterations than CASSCF optimizations require because of strong coupling between the orbital and CI parameters. In this paper we greatly accelerate the convergence by using an overshooting method based on the angle between successive parameter updates.

Potential energy curve of Cr₂: The potential energy curve of the chromium dimer is very challenging for state-of-the-art quantum chemistry methods for several reasons. The $^1\Sigma_g^+$ ground state of the molecule dissociates into two atoms in high-spin 7S states, each with 6 unpaired 3d and 4s electrons. Thus the molecule has a formal sextuple bond, and the minimal CAS space required for correct dissociation is CAS(12e,12o). Consequently, near-degeneracy correlation is very important, as evidenced by the fact that spin-unrestricted coupled cluster theory with single, double and perturbative triple excitations (UCCSD(T)) predicts a dissociation energy that is much too small²³. Simultaneously, dynamic correlation is also very important, as evidenced by the fact that CASSCF in a CAS(12e,12o) space gives a very weak minimum at a very large bond length. Thus, most of the calculations that have been performed employ CASPT2²⁴⁻²⁷ or the related n-electron valence state perturbation theory (NEVPT2)²⁸ to try to capture both near-degeneracy and dynamic correlation effects. These methods are sensitive to the choice of the CAS space, and in addition the CASPT2 method is sensitive to the choice of the ionization potential electron affinity (IPEA) shift. In fact, CASPT2 with a CAS(12e,12o) reference space and reasonable choices of IPEA shift yield well depths ranging from 1.1 to 2.4 eV²⁶. Since conventional CASSCF calculations are limited to about CAS(18e,18o), the density matrix renormalization group (DMRG)^{29,30} method has been employed^{24,28} as a CAS space solver, allowing the use of the larger CAS(12e,22o), CAS(12e,28o), and CAS(28e,20o) reference spaces, which partially cures this problem. Despite this, these methods have been unable to provide a definitive potential energy curve (PEC) for Cr₂.

Externally contracted multireference configuration interaction (MRCI) using determinants selected from a DMRG calculation in a CAS(12e,42o) as the reference space has also been used³¹. It gives a reasonably-shaped PEC shifted down by about 0.1 eV relative to experiment. Multireference averaged quadratic coupled cluster (MR-AQCC)³² is another accurate method that has been used to compute the PEC of Cr₂. It gives a well depth of 1.35 eV, and the shape of the PEC is in reasonable agreement with experiment.

Probably the most accurate method used for Cr_2 is the Auxiliary Field Quantum Monte Carlo (AFQMC)³³. Most AFQMC computations are performed using the phaseless approximation, the accuracy of which depends on the choice of the trial wavefunction. For Cr_2 , phaseless AFQMC is not sufficiently accurate with affordable trial wavefunctions. On the other hand free-projection AFQMC is exact (aside from statistical error), but very computationally expensive. So, a hybrid approach was used wherein free-projection AFQMC was performed in the 3z basis and the complete basis set correction was computed by adding in the correction from phaseless AFQMC for 3z, 4z, and 5z basis sets for $r < 2 \text{ \AA}$, and by adding in the correction from free-projection AFQMC with only 12 rather than 28 correlated electrons in 3z and 4z basis sets for $r > 2 \text{ \AA}$.

Part of the interest in Cr_2 comes from the fact that an experimentally deduced PEC is available which can be used to some extent to test the accuracy of theoretical methods. The shape of the PEC comes from high-resolution photoelectron spectra of Cr_2^- , which showed 29 vibrationally resolved transitions to the neutral Cr_2 ground state³⁴. However, there are gaps in the measured vibrational levels and the assignment of the higher levels is not unambiguous, so part of the PEC is not well constrained by the data. The vertical placement of the potential energy curve is determined from the dissociation energy. Experimental values vary considerably: 1.56(26)³⁵, 1.78(35)³⁵, 1.44(6)³⁶, 1.43(10)³⁷, and 1.54(6)³⁸ eV. We will use the last number in most of our plots, since it is more recent, but will keep in mind that it has considerable uncertainty. Since the zero point energy is 0.03 eV²⁴, the potential energy curves we present are shifted so that the well depth is 1.57 eV. Recently, the experimental data of Casey and Leopold³⁴ have reanalysed by Dattani³⁹ using a more flexible fitting function and a fully quantum mechanical treatment to obtain a slightly different PEC from the original. We show both of these curves in all our figures.

Hamiltonian: For the 3d transition metals it is important to include scalar relativistic effects, but the spin-orbit splitting is small. The two standard scalar relativistic Hamiltonians are the Douglas-Kroll and the $x2c$ ⁴⁰ Hamiltonians. In our work we employ mostly the $x2c$ Hamiltonian, but we have verified that the Douglas-Kroll Hamiltonian yields essentially the same PEC, though it gives a total energy for the molecule that is about 14.6 mHa higher. The 1- and 2-body integrals for the $x2c$ Hamiltonian are obtained using the PySCF package⁴¹.

Basis sets: Quantum chemists have designed several different sets of standard single-particle basis functions for most of the elements in the periodic table⁴². The ‘‘correlation consistent’’ bases of Dunning and coworkers⁴³⁻⁴⁵ are widely used and are designed to enable systematic extrapolation to the complete basis limit. These bases are designated cc-pVnZ, where n is referred to as the cardinal number of the basis set. They are designed for

non-relativistic calculations; the corresponding basis sets for relativistic calculations are designated cc-pVnZ-DK. We employ the cc-pVnZ-DK basis sets with n ranging from 2-5, and for brevity we designate these by 2z, 3z, 4z and 5z. These have 86, 136, 208 and 306 basis functions for the dimer, respectively, which result in the same number of orbitals written as linear combinations of the basis functions. In the SHCI calculations we allow excitations to and from all these orbitals, keeping only a small number of core, and in some calculations semicore, orbitals doubly occupied. By using more than one basis set, we can extrapolate the UCCSD(T) and SHCI energies to the complete basis limit making the usual assumption that the binding energy converges as the inverse cube of the cardinal number, n , for $n \geq 3$.

Cr_2 at a bond length of 1.5 \AA in the Ahlrichs SV basis⁴⁶ has become a very popular system for testing the accuracy and efficiency of electronic structure methods, even though this basis is much too small to give even a qualitatively correct potential energy curve⁴⁷. In the Supplementary Material⁴⁸, we provide accurate energies for this basis, both with and without core excitations.

Correlating 12 electrons: Molecular systems containing heavy atoms have orbitals with very different energies. Although core electron correlations make a large contribution to the total energy, they have only a relatively small effect on energy differences such as the potential energy curve (PEC) because the core contributions in the atoms and the molecule tend to cancel. In Cr, the 3d and 4s electrons are the valence electrons, the 3s and 3p electrons are semicore electrons, and the 1s, 2s and 2p electrons are the core electrons. Early calculations of Cr_2 employed only valence electron excitations; later calculations included also semicore electron excitations.

The computed energies depend not only on which orbitals are allowed to excite, but also on the nature of the orbitals that are kept frozen (not allowed to excite). Fig. 1 shows the PEC obtained from correlating only the 12 valence electrons by allowing excitations to all higher lying orbitals, keeping the semicore and core electrons fixed either in Hartree-Fock (HF) orbitals, or in orbitals obtained by optimizing in a CAS(12e,12o) space. The two curves differ greatly from each other and from the experimentally deduced PECs.

In Fig 2 we employ the 2z, 3z and 4z basis sets to study the basis set dependence of the PECs obtained again from correlating only the 12 electrons, using CAS(12e,12o) semicore and core orbitals. Although the PECs improve with increasing basis size, it is clear that correlating just 12 electrons is insufficient to get good agreement with experiment. This is in fact well known, but the precise PECs have not been published before.

Correlating 28 electrons: The coupled cluster method with single, double and perturbative triples (CCSD(T)) amplitudes gives very accurate energies for systems where a single determinant has a large amplitude, such as most

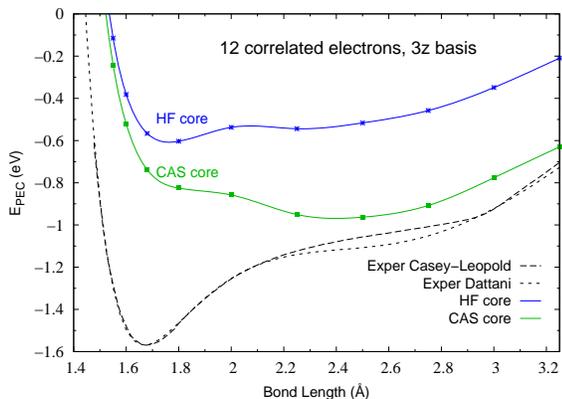


FIG. 1. Comparison of the SHCI potential energy curves correlating the 12 valence electrons with a HF core and a CAS core to experimentally deduced curves. Note that in the SHCI calculation excitations to all higher-lying orbitals are allowed. When correlating 12 electrons the nature of the frozen orbitals has a large effect on the PEC.

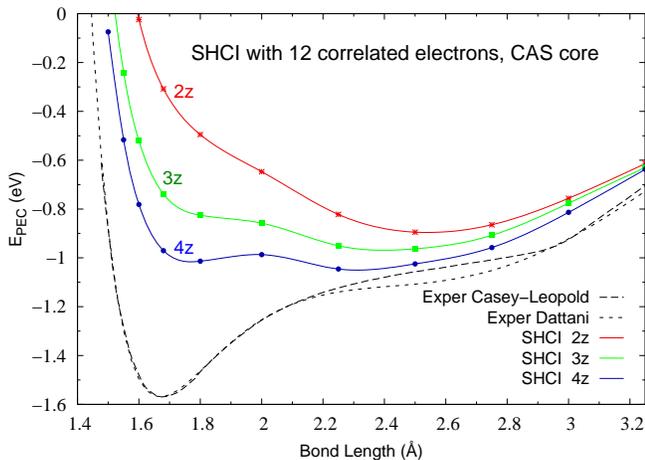


FIG. 2. Comparison of the SHCI potential energy curves, correlating the 12 valence electrons using a CAS core and 2z-4z basis sets, to experimentally deduced curves. It is apparent that correlating just the 12 valence electrons is insufficient to get an accurate PEC.

organic molecules at equilibrium geometry. Here we use the spin-unrestricted versions of HF and CCSD(T), denoted by UHF and UCCSD(T) respectively meaning that the HF up-spin and down-spin orbitals, and the CCSD up-spin and down-spin amplitudes, need not be the same, since this allows for dissociation of the molecule into two high-spin atoms. On the other hand, in our SHCI calculations, up- and down-spin orbitals are the same, so that the SHCI wavefunction can be an eigenstate of S^2 . In Fig. 3 we show the PECs obtained from UCCSD(T) using PySCF⁴¹ and 2z through 5z basis functions. Of course, the total energies go down monotonically with increasing

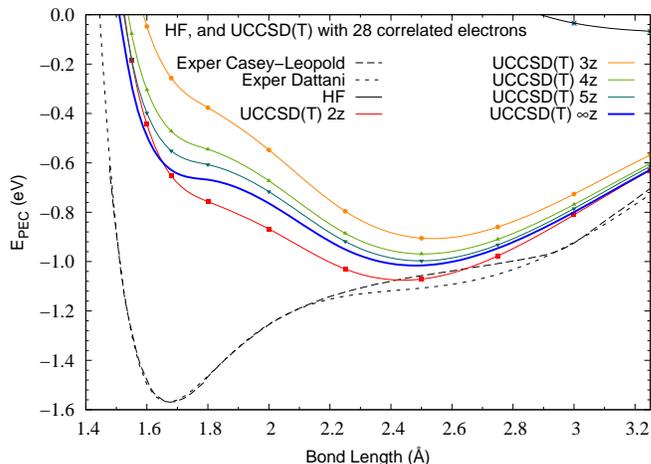


FIG. 3. UHF and UCCSD(T) potential energy curves correlating 28 electrons in bases ranging from 2z to 5z, and the complete basis limit. Note that the 2z curve lies lower than the 3z, 4z over the entire range, and lower than the 5z and complete basis curves over most of the range.

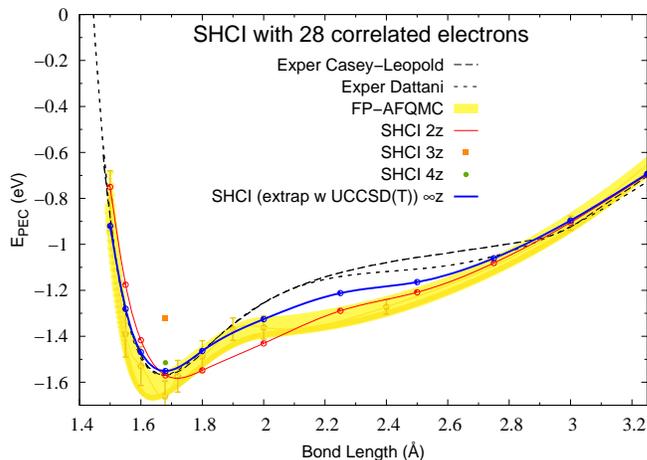


FIG. 4. Comparison of the SHCI potential energy curves correlating 28 electrons to experimentally deduced curves. The red curve is for the 2z basis, the orange dot for the 3z basis, the green dot for the 4z basis and the blue curve is the complete basis limit using the correction from UCCSD(T). Similarly to UCCSD(T), when 28 electrons are correlated, the binding energies do not change monotonically with the basis cardinal number. The FP-AFQMC curve from Fig. 4 of Ref. 33 is also shown.

basis size, but very surprisingly the 2z PEC curve lies lower than the 3z, 4z and 5z curves. The same behavior is observed also in SHCI calculations at equilibrium with 2z, 3z, and 4z bases. The infinite basis extrapolated UCCSD(T) curve, shown as the solid blue line lies below the 2z curve at short distances and above the 2z curve at large distances. The extrapolation is done using the 4z

and 5z curves, but almost the same extrapolated curve is obtained from 3z and 4z curves. The 28 correlated electron UCCSD(T) curves have shapes similar to those from the 12 correlated electron SHCI curves, but they agree even less well with experiment.

Although UCCSD(T) gives poor PECs, it can be used to provide a reasonable basis set correction to the SHCI curves that we present next. The accuracy of the correction has been checked at the equilibrium bond length, where we find that the correction to the 2z SHCI energy, using the (3z,4z,5z) UCCSD(T) energies agrees with that obtained from the (3z,4z) SHCI energies within 0.1 eV. More precise agreement cannot be expected since the uncertainty of the SHCI 3z, 4z energies from the extrapolation in ϵ_1 is itself about 0.1 eV. The 4z SHCI calculations with 28 correlated electrons have a Hilbert space of $(^{198}C_{14})^2 \approx 10^{42}$. One of the desirable features of the SHCI method is that although the Hilbert space increases by 10 orders of magnitude going from the 2z to the 4z basis, the cost of the calculation is only a few times larger. This desirable feature is even more evident when the increase in Hilbert space size comes from correlating additional core orbitals. However, since the 2z calculations are already expensive, we have done the larger basis calculations only at equilibrium.

The PEC from SHCI in the 2z basis, correlating the 28 valence and semicore electrons is shown as the red curve in Fig. 4. The blue curve is the PEC extrapolated to infinite basis size using the correction from UCCSD(T). It has a minimum of -1.55 eV at 1.679 Å, in agreement with the experimentally determined -1.57 eV³⁸ at 1.679 Å³⁴. It agrees very well with experiment at bond lengths around equilibrium and also at long bond lengths. It differs a little from experiment in the shoulder region from 1.8 to 2.7 Å, which roughly coincides with the range

of distances where the experimentally deduced curve is most uncertain because of missing vibrational levels, as also noted in Ref. 33. This is also the region where the computed energies converge most slowly. The blue curve agrees well also with the curve labeled FP-AFQMC in Fig. 4 of Ref. 33, except that the FP-AFQMC curve is yet a bit lower than SHCI in the shoulder region.

Conclusions: The SHCI method enables systematic convergence to the exact energy for moderately strongly correlated systems with sizes of Hilbert space that were previously inaccessible. We have demonstrated its power by computing the potential energy curve of a very challenging molecule, Cr₂. The size of the largest Hilbert space treated with SHCI is 10⁴² determinants. Nevertheless, energies estimated to be accurate to a few milliHartrees were obtained from calculations that involve 10⁹ variational determinants or fewer, and several trillion perturbative determinants. In future work we plan to use an effective Hamiltonian that incorporates the effect of explicit interelectronic correlation⁴⁹ to reduce the magnitude of the basis set extrapolation error.

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¹ We note that the usual quantum chemistry definition of weak correlation requires that much of the amplitude resides on a single state. Hence some systems that we consider in this paper to be weakly correlated, would count as being strongly correlated in the quantum chemistry literature.

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

Junhao Li,¹ Yuan Yao,¹ Adam A. Holmes,^{1,2} Matthew Otten,¹ Qiming Sun,^{3,4} Sandeep Sharma,² and C. J. Umrigar¹

¹*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853, USA*

²*Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, CO 80302, USA*

³*Tencent America LLC, Palo Alto, CA 94036, USA*

⁴*Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, CA 91125, USA*

ENERGY CONVERGENCE IN AHLRICHS SV BASIS

For Cr₂, 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, Cr₂ 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 $E_{\text{var}} - E_{\text{tot}}$. In Figs. 1 and 2 the solid lines are weighted quartic fits, using $1/(E_{\text{var}} - E_{\text{tot}})^2$ 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_{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_{var} and E_{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_{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,

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

where $e_{\text{HF},i}$ 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_{det} .

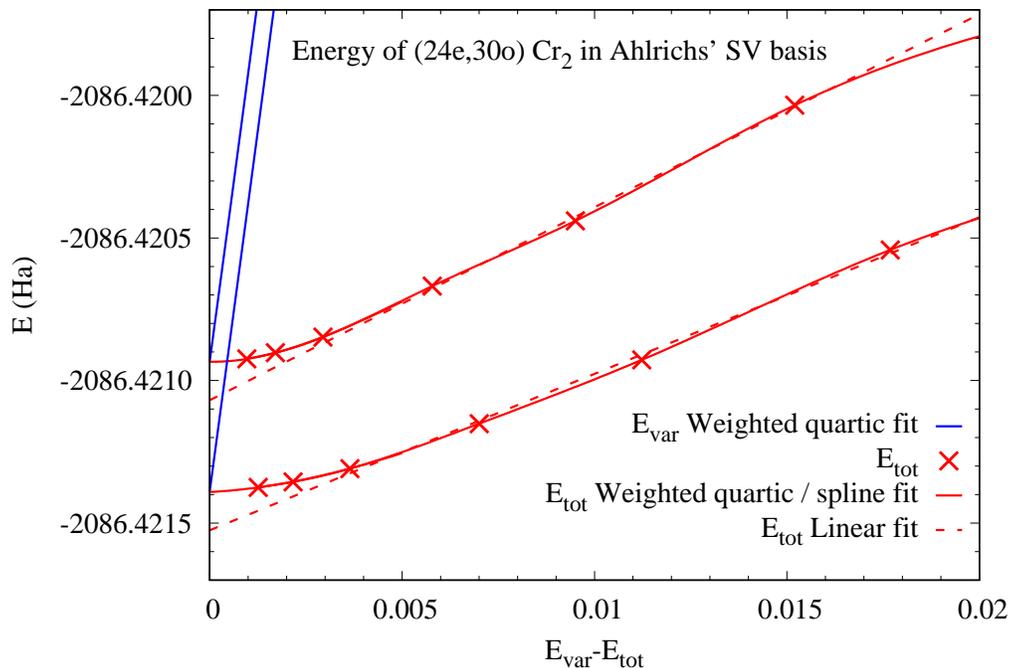


FIG. 1. Convergence of the frozen Mg-core (24e,30o) total and variational energies. The upper pair of curves freeze the core in HF orbitals and the lower pair in CAS(12,12) natural orbitals.

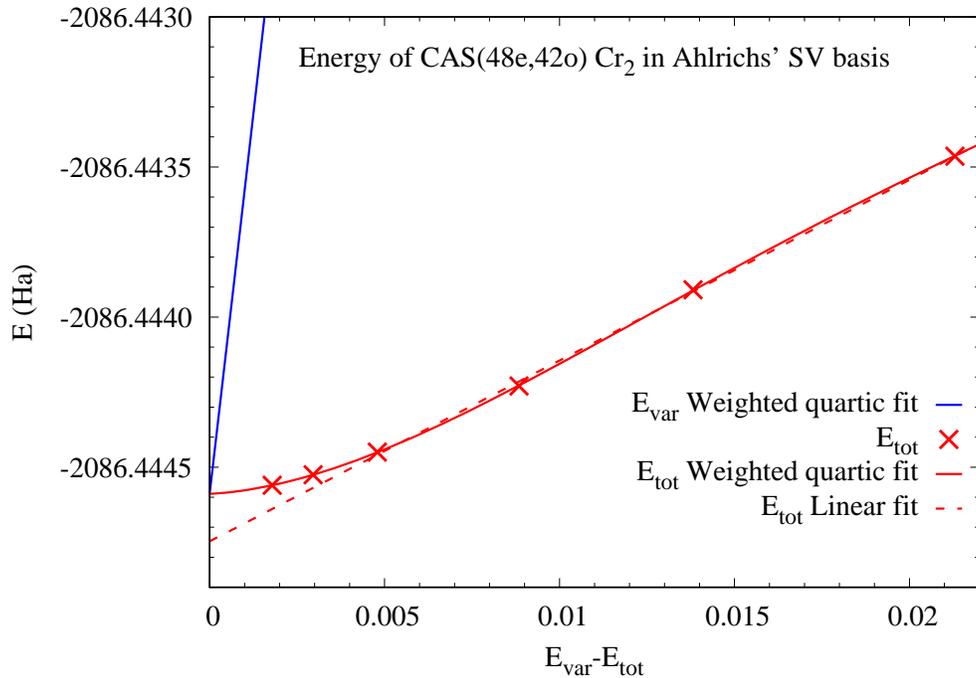


FIG. 2. Convergence of the all-electron (48e,42o) total and variational energies.

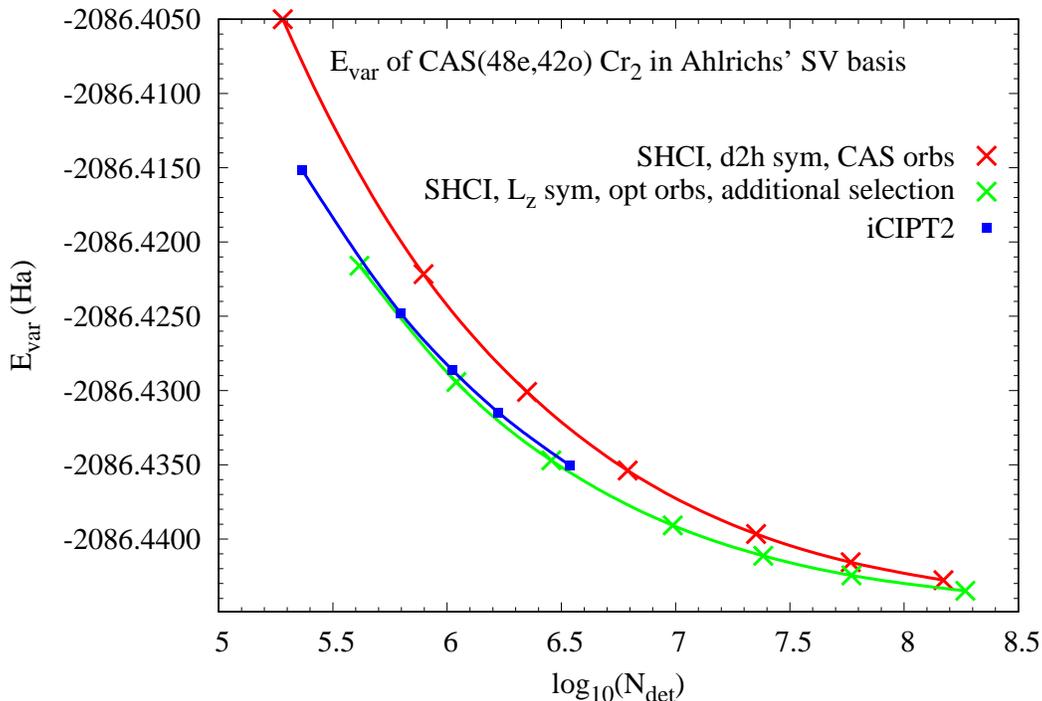


FIG. 3. Demonstration of improvement in convergence of the (48e,42o) variational energy upon using L_z symmetry, optimized orbitals and the additional selection criterion. The iCIPT2 energies of Ref. 14 are also shown.

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 L_z 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 $r=1.5 \text{ \AA}$, 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_{det} is the number of determinants in the variational wavefunction. The estimated statistical and/or extrapolation errors in the last digit(s) of E_{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.

ϵ_1 (Ha)	N_{det}	Energy + 2086 (Ha)		Real time (sec)	
		E_{var}	E_{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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