Multireference Configuration Interaction Calculations on Cr_2: Passing the One Billion Limit in MRCI/MRACPF Calculations

Holger Dachsel, Robert J. Harrison,* and David A. Dixon*

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 906 Battelle Blvd., MS K1-83, Richland, Washington 99352

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The region around the minimum of the potential-energy curve of Cr_2 has been calculated at the multireference configuration interaction (CI) level including almost 1.3 billion configurations in the CI calculation. The computational techniques as implemented on massively parallel computers which enabled this calculation are described. The calculated results are $R_e = 1.72$ Å, $D_e = 1.09$ eV, and $\omega_e = 338.7$ cm^{-1} as compared to experimental values of $R_e = 1.679$ Å, $D_e = 1.50 \pm 0.05$ eV, and $\omega_e = 452.34(\Delta G_{1/2})$ cm^{-1}. The error of 0.4 eV in the dissociation energy can be attributed to relativistic effects following other authors (0.2 eV) and the need for higher angular momentum basis functions in the one-particle set (0.2 eV).

Introduction

The dimer of chromium, Cr_2, has been a notoriously difficult molecule to treat computationally and is one example of the difficulties found in providing theoretical treatments for molecules containing first-row transition-metal atoms.[1] The Cr atom is high spin, $d^5s(^7S)$ and dimerizes to form a low-spin molecule ($^1\Sigma_g^+$) with the bonding molecular orbitals fully occupied (σ_g^2, σ_g^2, π_u^4, δ_g^4), which would correspond to a "formal" hextuple bond. The ground state has been established by rotationally resolved measurements of the A ← X transition.[2,3] The vibrational frequency is relatively high at 452 cm^{-1}, consistent with the formal high bond order, as is the quite short bond length of 1.679 Å.[3] A modified RKR (Rydberg−Klein−Rees) potential energy curve for Cr_2 has been developed based on negative-ion photoelectron spectroscopy of Cr_2^- and shows interesting structural features, notably a "shelf" region at higher vibrational energy levels.[4] However, the binding energy is not all that high for such a hextuple bond, with the best experimental value giving 1.44 ± 0.05 eV.[5]

The restricted Hartree−Fock method predicts that Cr_2 is unbound by 20 eV, reminiscent of the problems with the molecule F_2.[6] Goodgame and Goddard,[7] by using generalized valence bond (GVB) wave functions, originally suggested that the experimental results were wrong as they predicted a low D_e of 0.3 eV and a very long value for R_e of 3.0 Å. They recalibrated their method using a semiempirical correction of the self-Coulomb repulsion energy.[8] This led to $R_e = 1.86$ Å and $D_e = 1.86$ eV, in better agreement with experiment, although the bond distance is too long and the well-depth is too deep, an odd combination. Use of a complete active-space self-consistent field (CASSCF) wave function with 3088 configurations still leads to a structure that is unbound by ~1.6 eV.[9] Walch and Bauschlicher[10] employed an approximate additive scheme and generated a qualitatively reasonable curve with $R_e = 1.78$ Å, $\omega_e = 383$ cm^{-1}, and $D_e = 0.71$ eV. With a similar CAS starting wave function, Werner and Knowles[11] performed an internally contracted multireference configuration interaction (MRCI) calculation and obtained a negative binding energy of −0.03 eV. Roos and co-workers[12] performed CASSCF/CASPT2 (second-order perturbation theory with the CAS wave function) calculations and found $D_e = 1.54$ eV, $\omega_e = 535$ cm^{-1}, and $R_e = 1.69$ Å, but there are issues with the calculations due to the appearance of intruder states and the sensitivity of the results to the zeroth-order Hamiltonian. By using a symmetry-broken (C_{2v}) UHF wave function and calculations at the UCCSD(T) (unrestricted coupled cluster with single and double excitations and a perturbative correction for triples) level, Bauschlicher and Partidge[13] obtained $D_e = 0.89$ eV but the bond distance is far too long at 2.54 Å. In recent work attempting to eliminate the intruder state problem, Mitrushenkov and Palmieri[14] used a second-order perturbation energy treatment of the CAS wave function with a modest size 10s8p3d1f basis set and obtained $R_e = 1.626$ Å, $\omega_e = 647$ cm^{-1}, and $D_e = 2.53$ eV.

In the most recent study, Stoll and Werner[15] used the MRACPF[16] (multireference averaged coupled-pair functional) approach based on the 3088 configuration CAS wave function to obtain $D_0 = 1.12$ eV, $r_e = 1.73$ eV, and $\Delta G_{1/2} = 318$ cm^{-1}. They, however, had to use an incremental scheme to estimate the size of the correlation correction due to the 3s and 3p orbitals. At the CASSCF (12/12) level with a 7s6p5d2f1g basis set, these authors found that Cr_2 was unbound by 1.50 eV with respect to the RHF atoms at $R = 1.68$ Å. They then reduced the 28 784 CSFs to a 3088-CSF (configuration state functions) reference wave function, which led to an increased instability of 1.66 eV. At the MRACPF level with ~3 million singly external CSFs, they found that Cr_2 was now bound by 0.18 eV. An internally contracted wave function also including double excitations led to a value for D_e of 0.37 eV. These authors then investigated basis-set improvements and found that five sets of f orbitals account for 0.74 eV of binding and three sets of g orbitals accounts for 0.28 eV of binding. They suggest that h functions may contribute up to 0.2 eV (a single h function accounts for 0.08 eV). They also found that relativistic corrections were on the order of 0.18 eV for the binding energy, essentially the same as the 0.19 eV correction of Roos and co-workers.[12]

There have also been a large number of density functional theory (DFT) calculations on the Cr_2 dimer.[1,13,17,18,20] At the Xα level,[17] a long, weak bond was found, in agreement with

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the original work of Goodgame and Goddard. A number of calculations have been done at the local DFT (LDFT) level.[18] A number of different local functionals were used, but with the Vosko, Wilk, and Nusair correlation functional,[19] the potential-energy curve near the minimum is accurately predicted; the LDFT method predicts overbinding by 1.2 eV. Gradient-corrected functionals give results ranging from 0.9 to 1.75 eV for D_e.[1,20] Calculations at the restricted B3LYP level give a short value for R_e (1.56 Å) and an unbound dimer, whereas at the unrestricted level, R_e (2.51 Å) is too long and D_e (0.98 eV) is too low.[13] If the BLYP functional is used at the unrestricted level, a good value for R_e (1.70 Å) is found but D_e (1.99 eV) is too large.[13]

Our laboratory is interested in calculating molecular properties rigorously by using ab inito methods without the use of empirical corrections.[21−23] Our approach for molecules containing first- and second-row atoms has been to use CCSD(T) based on HF wave functions with correlation-consistent basis sets[24] and then extrapolating to the complete basis-set limit. However, this is not necessarily the appropriate way to address transition-metal compounds. In the first place, correlation-consistent basis sets are not yet available for transition-metal compounds and as noted above CCSD(T) methods have yet to be shown to provide reliable results for molecules such as Cr_2. Thus, we have decided to calculate the properties of Cr_2 by using the MCSCF method followed by a single and double CI from the MSCF reference space. We have not made any approximations in the CI due to the availability of large massively parallel prcoessing computer systems and an efficient CI code for such computers.[25]

Calculations

The calculations were done with the contracted (20s15p10d6f)/[9s8p7d5f] Cr basis set of Bauschlicher and Partidge.[13] We employed the MCSCF reference wave function originally developed by Walch et al.[9] and used by Werner and Knowles[11] and Stoll and Werner.[15] There are the 3088 reference configurations in this wave function, which is developed as follows. There are exactly two electrons in each of the 3dδ, 3dδ', 3dπ, and 3dπ' orbital subsets, and four electrons are in the (3dσ, 4sσ) subset. This is a reduction of the complete 12/12 CAS wave function based on the Cr 3d and 4s orbitals. For the CI calculations, we also included the 3p core orbitals. All singles and doubles within the interacting space restriction are used based in the ACPF formalism.[16] With this basis set and this wave function, there are 1.3 billion configuration state functions (CSFs) in the calculations. All calculations were done with the parallel version of the COLUMBUS program system.[25]

Computational Aspects

The calculations were carried out by using 128 processors on the EMSL-IBM/SP. Each processor was equipped with 128 MB (B = byte) of memory, and the peak performance of each processor is 480 Mflops. IBM's implementation of active messages in a multithreaded operating system allows a bandwidth up to 100 MB/s and a latency of 90 μs. The memory on each processor is used to satisfy the requirements for workspace, virtual disk, and for the global arrays (89 MB). All off-diagonal integral files are stored locally on the virtual disks. These intergal files are relatively small (8.9 MB) but are very frequently accessed. The memory requirement for the virtual disks are taken from the file size of these integral files.

To calculate the matrix vector product within the standard Davidson method, four vector segments have to be kept in local memory and the workspace is used for this purpose. The amount of available workspace determines the amount of interprocessor communication and I/O if the expansion and product vectors are stored on disk. The more workspace that is available, the less communication and I/O there are. In the chromium dimer caculations, we used 63 MB as workspace, which gave 676 segments for a CI dimension of 1 295 937 374. Each segment includes about 1.93 million configuration state functions.

The COLUMBUS CI program[25] computes the matrix vector product in a single loop over segment pairs (tasks) instead of a double loop over segments. This implementation provides more flexibility with regard to the dynamic load balancing. The single loop over segment pairs is driven by a time-sorted task list and by a task skip vector. The tasks are ordered according to execution times to achieve the best possible granularity and avoid processors from being idle. If both expansion vector segments for a given task are zero or if a task does not give any contribution to the product vector, the task is skipped. According to the task skip vector, 151 765 of 278 610 tasks (54.5%) were skipped per iteration.

Seventeen megabytes per processor were used to store all global arrays, which include the index vectors, distinct row tables, integral files, and expansion and product vectors. The diagonal elements of the Hamiltonian and the coupling coefficients (GUGA loops) are calculated "on-the-fly" if needed. The expansion and product vectors are stored in one global array. The index vectors, distinct row tables, and integral files alone required 16 MB per processor. The remaining memory of 1.1 MB per processor was used to store all the expansion and product vectors. Thus, on the 128 processors, only 146 MB were available to store these vectors. Each vector is of dimension 1 295 937 374, leading to a requirement of 10.4 GB of global memory. The convergence behavior of the Davidson method depends on the dimension of the subspace. A reasonable convergence requires a subspace dimension of 8; thus, 16 vectors (8 expansion vectors and 8 product vectors) had to be stored. Data compression[26] has been used to reduce the amount of data, significantly leading to a savings of a factor of about 25. Major improvements to the algorithm in ref 26 have been made to improve the efficiency of the compression scheme. The compression schemes for the expansion vectors as well as for the product vectors are adjusted dynamically. Information about the structure of the eigenvectors is used to eliminate completely obsolete data. If the absolute value of an eigenvector component u_i is less than the absolute error Δu_i calculated at the beginning of the Davidson procedure, where information about the structure of the eigenvectors is not yet available, Δu_i is replaced by $f_i \Delta u_i$ where $f_i = |u_i/\Delta u_i|$. Even if compression is used, the vectors could not be kept in memory. A recently implemented shared-file toolkit was used to store the data on disk. The shared file uses the local scratch disks (2 GB) on each processor. The file is striped over the local disks. This shared file system allows each processor to be able to access any location in the file independently. The total amount of data being sent over the network is about 6 Tb per iteration.

A typical iteration took about 8990 s of wall time and 8888 s of CPU time on 128 processors for a CPU utilization of ~99%. About 25 iterations are necessary for convergence (an energy threshold of 0.01 mH). Usually, MR-ACPF caculations need about 50% more iterations than comparable MR−CI calculations. The program measures the timings for reading the integrals, reading the expansion vector, and updating the product vector during the matrix vector multiplication, which consumes most of the computation time. The expansion vector is stored on the local disks in compressed form. An I/O bandwidth of 4

TABLE 1: Data Transfer Information

process	no. of bytes	time (s)	bytes/s
Data Transfer (aggregate)			
reading integrals	274.4 G	4149	66.1 M
reading expansion vector	3579.6 G	36712	97.5 M
updating product vector	2300.3 G	197003	11.7 M
total	6154.3 G	237864	25.9 M
Data Transfer (per processor)			
reading integrals	2.1 G	32.4	66.1 M
reading expansion vector	28.0 G	286.8	97.5 M
updating product vector	18.0 G	1539.1	11.7 M
total	48.1 G	1858.3	25.9 M

TABLE 2: Total Energies as a Function of R for Cr_2 at the MRACPF Level

R (au)	R (Å)	energy (au)
3.00	1.588	−2087.49257
3.125	1.654	−2087.50002
3.175	1.680	−2087.50134
3.2126	1.700	−2087.50217
3.25	1.720	−2087.50255
3.50	1.852	−2087.50227
4.00	2.117	−2087.50094
2Cr		−2087.46249

TABLE 3: Summary of Results for Cr_2

method	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	D_0 (eV)
this work	1.72	1.09	338.7	1.05
expt	1.679[a]	1.50 ± 0.05	452.34 ($\Delta G_{1/2}$)[a]	1.44 ± 0.05[b]

[a] Reference 3. [b] Reference 5.

MB/s and a compression factor of 25 give an effective transfer rate of about 100 MB/s. Updating the product vector is more complex than reading the expansion vector as it includes reading the decompressed data, decompression, local accumulation, compression, and writing the compressed data. The speed for updating is the harmonic mean. The time due to processor locks in the update process is also included. There were 1858 of the 8990 s (21%) consumed for data transfer per iteration. The remaining 7132 s (79%) are mainly spent in BLAS routines and for computing the coupling coefficients (GUGA loops). Only about 10% of the 7132 s are used for computing the coupling coefficients. Information about the data transfer rates is summarized in Table 1.

Results and Discussion

The total energies are given in Table 2, and the summary results are given in Table 3 where they are compared to the experimental values. The optimized bond distance is too long by 0.04 Å, and the dissociation energy is too low by 0.4 eV. The frequency is too low by ~110 cm^{-1}. Two previous studies[12,15] have both shown that the relativistic correction is 0.18−0.19 eV (at the experimental R_e) based on pseudopotential calculations with and without relativistic corrections[15] and on scalar-relativistic mass−velocity and Darwin terms at the CASPT2 level.[12] Inclusion of relativistic corrections would raise our calculated dissociation energy (D_0) to 1.23 eV, an error of 0.2 eV (4.6 kcal/mol) or 13.9%. The remaining source of the error in D_e can come from basis-set incompleteness or from the need to correlate the 3s orbitals.

Another molecule that has multiple bonds that dissociates to a high-spin species is N_2 ($^1\Sigma_g{}^+$) going to 2N (^4S). At the CAS-CI level[27] with a cc-pVDZ basis set, the error in D_e is 26.4 kcal/mol out of the experimental value[28] of 228.4 kcal/mol (an 11.6% error); at the CCSD(T) level, the error is 27.6 kcal/mol (a 12.1% error). With the cc-pVTZ basis set, the error is 10.6 kcal/mol at the CAS-CI level for an error of 4.6%, and even with the cc-pVQZ basis set, the error is still 4.4 kcal/mol or 1.9%.[27] Obviously, it is very difficult to reach the complete basis-set limit for multiply bonded systems. Our basis set is probably close to being saturated in the s, p, d, and f spaces, but clearly we do not have any higher angular monmentum functions than f functions. As shown for N_2, higher angular momentum functions are important in getting an accurate bond energy for multiply bonded diatomics. We thus expect that the remaining error for Cr_2 is due to the lack of g- and h-type functions, but given the relatively saturated s, p, d, and f basis set that we are using, these corrections are on the order of 0.2 eV. This is in sharp contrast to the results found by Stoll and Werner[15] based on a more approximate CI who suggest that g functions account for 0.28 eV of the binding energy and that h and higher angular momentum functions account for up to 0.2 eV. Clearly these estimates are too high. We also note that the CAS-CI/cc-pVDZ value[27] for the bond distance in N_2 is 1.120 Å, as compared to the experimental value of 1.098 Å,[28] an error of 2.0%, quite comparable to our error of 0.04 Å or 2.4%.

The calculated curve for Cr_2 is too flat, and we predict a stretching frequency that is too low. The elegant negative-ion photoelectron spectroscopy work of Casey and Leopold[4] allowed these authors to construct a potential-energy curve based on the RKR method. The RKR curve clearly has a "shelf" starting at about $R = 2.2$ Å and 3000 cm^{-1} (8.6 kcal/mol or 0.37 eV) above the minimum. In this region the potential is much flatter and rises more slowly than in the region near R_e or for R larger than 3.0 Å. The energy at which the potential becomes flat is just about the error in our calculated D_e (or D_0), 0.4 eV. Thus, we feel that the following description is appropriate for the Cr_2 curve. In the region of the minimum, which is dominated by the multiple bond, there is a large relativistic effect stabilizing the bond and there are significant contributions of higher angular momentum functions to the bond energy. As the bond lengthens, the d−d overlap is quickly lost and 4s−4s bonding becomes dominant as well as changes in the interactions of the d orbitals on the various centers. At longer R, it is likely that the d orbitals become more atomic high-spin-like and now only interact via an antiferromagnetic interaction. In this region, there is apparently a smaller relativistic correction and the role of the higher angular momentum functions in the basis set is smaller due to the smaller overlap of the d orbitals. Thus, at longer R, our approach is more accurate than at shorter R and the curve is flatter as we find.

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