

THE GROUND STATE POTENTIAL FOR THE CHROMIUM DIMER REVISITED

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It is a great pleasure to dedicate this paper to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays. The connections between the University of Lund and the quantum chemistry groups in Prague and Bratislava is long-lasting and we in Lund have highly appreciated the scientific collaborations with these research groups.

Results are presented from a new theoretical study of the ground state potential curve of the chromium dimer using multiconfiguration second-order perturbation theory. A new basis set of the atomic natural orbital type is used where the construction includes correlation of the semi-core 3p orbitals and scalar relativistic effects are added using the Douglas-Kroll Hamiltonian. The active space used in the CASSCF/CASPT2 calculations comprised 16 orbitals with 12 active electrons. The resulting ground state potential is in agreement with experiment. Computed spectroscopic constants are (with experimental values within parentheses): $R_e = 1.66$ (1.68) Å, $D_0 = 1.65$ (1.53 ± 0.06) eV, $\Delta G_{1/2} = 413$ (452) cm⁻¹. Higher vibrational frequencies are also well reproduced.

Keywords: Chromium; CASSCF/CASPT2 method; Perturbation theory; *Ab initio* calculations; Basis set; Hamiltonian.

The chromium dimer has become a challenging test case for a variety of computational methods that attempt to describe systems where the electronic ground state is highly multiconfigurational (the weight of the closed-shell Hartree-Fock configuration is only 45% at the equilibrium geometry). The difficulty to describe the potential curve using multireference CI (MRCI) methods has been noted^{1,2}. The most extensive of these studies, the MRACPF calculation of Dachsel *et al.*² uses more than a billion configurations. Still only 66% of the binding energy is obtained and the bond distance is 0.04 Å longer than experiment. That coupled cluster theory cannot describe the binding is less surprising³, considering that highly excited configurations play an important role in the wave function.

The molecule has been used to test the performance of the complete active space SCF (CASSCF) method⁴ in conjunction with multiconfigurational second order perturbation theory (CASPT2) for the treatment of dynamic correlation effects⁵⁻⁷. The CASSCF wave function with the Cr 3d and 4p orbitals active and 12 active electrons, should give a qualitatively correct description of the wave function for all bond lengths. However, it was already shown in 1982 that such a wave function will not lead to a bound molecule⁸. The dynamic correlation effects are too large. A first attempt to use the CASPT2 method to account for these effects was made in 1994⁹. This calculation turned out to be a severe test of the CASPT2 method. A large number of intruder states appeared along the potential curve and deteriorated the result. However, with these intruder states removed, it was still possible to compute the spectroscopic constants of Cr₂ with a surprisingly high accuracy. The bond energy was determined to be 1.55 eV with a bond distance of 1.71 Å. The corresponding experimental values are 1.53 eV¹⁰ and 1.68 Å¹¹, respectively. The general shape of the potential curve was also reproduced with the typical plateau region where the 4s bond is formed. The computed force constant was, however, too large leading to a vibrational frequency about 100 cm⁻¹ larger than experiment.

Using a modified form of the zeroth order Hamiltonian in the CASPT2 method¹², Andersson was later able to make a detailed study of a large number of excited states¹³. The intruder state problem, however, was not solved. In 1995, a level shift technique was introduced, which made it possible to remove the intruder states from the first-order wave function and produce stable second-order energies¹⁴. Potential curves for the ¹Σ_g⁺ and ¹Σ_u⁺ states of Cr₂ were used to illustrate the approach. These calculations gave smooth potential curves and spectroscopic constants in agreement with experiment for both states. The importance of including 3s,3p correlation and relativistic effects was illustrated as well as the importance of the basis set superposition errors (BSSE) with the basis sets used. Some time later Forsberg and Malmqvist demonstrated the use of an imaginary level shift to account for the intruder state problem¹⁵. Again, the potential curve for Cr₂ was used as an illustration and it was shown that the computed binding energy depends on the size of the applied level shift. This dependence, however, was not larger than 0.1 eV for realistic values of the level shift. Angeli *et al.* have recently introduced a contracted variant of multiconfigurational second-order perturbation theory¹⁶. They applied it to the Cr₂ ground state potential curve and showed that the contraction removes the problem with the intruder states without deteriorating the results.

However, these earlier studies are afflicted by errors due to the choice of the basis set and the treatment of relativistic effects. A large BSSE correction to the binding energy was obtained with the basis set used in the work of Roos and Andersson¹⁴ even if an attempt was made to enlarge the basis set in the 3s,3p region. Scalar relativistic effects were introduced only at the lowest level using perturbation theory with a non-relativistic basis set.

Work has recently started, where new basis sets of the atomic natural orbital type (ANO) are developed for the entire periodic system. These basis sets will be introduced into the basis set library of the program system MOLCAS¹⁷. They will be constructed using the Douglas–Kroll Hamiltonian¹⁸ to account for scalar relativistic effects. The semi-core electrons are included in the correlation treatment (3s,3p for first row transition metals). The ANOs are obtained from an average density matrix obtained from CASPT2 calculations on a number of electronic states of the atom and its positive ion. Here, we shall illustrate the use of the new basis set for the Cr atom by a new set of calculations of the chromium dimer.

COMPUTATIONAL

The Basis Set

CASSCF/CASPT2 calculations were performed on the d^5s , 7S , d^4s^2 , 5D states of the chromium atom and the d^5 , 6S state of the positive ion with the 21s15p10d6f4g primitive basis set of Pou *et al.*¹⁹ Scalar relativistic effects were included using the Douglas–Kroll modification of the one-electron Hamiltonian. The 3d and 4s electrons were active and the 3s,3p shells were included in the correlation treatment at the CASPT2 level.

The first calculations used six active orbitals: 3d and 4s. An intruder state, however, appeared in the CASPT2 calculations on the ground state. The active space was therefore extended with a second 3d shell. With this active space (six (five) electrons in 11 orbitals, 6(5)/11), the IP was computed to be 6.91 eV to be compared to the experimental value 6.76²⁰. The ${}^7S \rightarrow {}^5D$ excitation energy was 1.26 eV which is 0.26 eV larger than experiment²⁰. The error reflects the difficulty to saturate the active space for transition metals. A test was made where the 4p orbitals were added to the active space, but this hardly affected the relative energies at all. The errors are thus most probably inherent to the second-order treatment of the dynamic correlation effects. It is unlikely that the basis set is too small.

The three CASPT2 density matrices obtained with the 6(5)/11 active space were averaged with equal weights. The ANOs were obtained as the corre-

sponding eigenfunctions. All ANOs with occupation numbers larger than 10^{-6} can be used, resulting in a maximum contracted set of the size: 10s10p8d6f4g. Note that these orbitals are ordered by the occupation numbers, with the most important orbitals first. This may be of significance when selecting a reduced set for molecular calculations. Here the set 9s8p7d5f3g was used for the chromium dimer.

The Active Space

Traditionally the chromium dimer has been treated with an active space comprising the 3d and 4s orbitals of the two atoms (12 electrons in 12 orbitals). As described above, this active space will lead to severe intruder-state problems, which have to be treated using a large level shift. The use of a modified zeroth-order Hamiltonian, as introduced by Andersson¹², only partly reduces this problem. This modification introduces an extra stabilization of the active orbitals with occupation numbers lower than two such that their energies more resemble ionization energies. For details, we refer to the paper by Andersson¹². Three such modifications were suggested, labeled *g1*, *g2*, and *g3*. Here, *g1* has been used.

With the new basis set, it turns out that the intruder-state problems are even more severe. They come mainly from 4p-derived orbitals. An analysis of the CASPT2 wave function showed that the most severe intruder states could be removed if the active space was extended to sixteen orbitals, adding to the 3d,4s set two orbitals of σ_g symmetry and one pair of π_u orbitals. The resulting CASSCF wave function is then not completely size-consistent because bonding orbitals are not balanced with antibonding. The occupation of these, however, are very small. Furthermore, at large distance the occupation of the extra orbitals are also small (0.0004, 0.0017, 0.0016, 0.0016). The number of CSFs in the CASSCF wave function is 1 774 172 (8 018 562 determinants). This active space also gives rise to intruder states in the CASPT2 wave function, but they are now much weaker (one orbital in each of the symmetries 1, 2, and 3 were involved). A level shift of 0.3 was used to remove these intruders.

The Potential

Calculations were performed for 38 points along the potential ranging from 1.38 to 50 Å. A cubic spline fit was used between these points. The numerical Schrödinger equation was solved to obtain the rotation-vibration spec-

trum. The module VIBROT in the program system MOLCAS was used for this purpose.

Calculations were also performed on one Cr atom with the basis set of the other atom present. An 3d,4s active space was used. The results were used to correct the results for Cr₂ for the basis set superposition error using the full counterpoise method.

RESULTS AND DISCUSSION

The Ground State Potential for Cr₂

Figure 1 shows the CASSCF and CASPT2 potentials with and without the counterpoise correction. There is an interesting difference between the present CASSCF results and the earlier potentials obtained with the 3d,4s active space. These potentials were totally repulsive, except for a very shallow minimum at large distances. With the 4p orbitals present in the active space, we obtain a pronounced minimum in the 4s bonding region. This improvement in the CASSCF potential is important for the CASPT2 results. Earlier results gave a too large force constant in the 3d region and a too sharp transfer between this part and the 4s bonding part of the potential. The present potential has a smoother transfer, which leads to better agreement with experiment for the force constant and vibrational levels. We

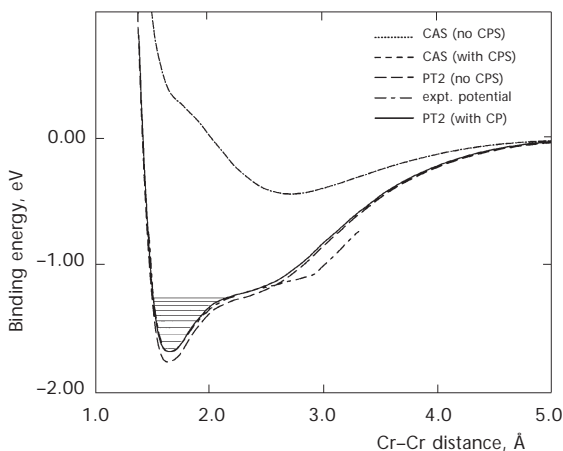


FIG. 1

The CASSCF and CASPT2 ground state potentials for Cr₂ with and without counterpoise correction for BSSE

conclude that an accurate description of the Cr_2 ground state potential needs to include 4p derived orbitals in the active space.

The effect of BSSE on the CASSCF potential is so small that it is not visible in the figure. The effect is larger at the correlated level, as expected, but much smaller than in the earlier calculation by Roos and Andersson¹⁴, where the contribution to the binding energy was 0.30 eV. Here it is reduced to 0.08 eV. The computed spectroscopic constants are presented in Table I, where they are compared to the experimental data.

The first measurements of the bond energy (D_0) reported a value of 1.44 ± 0.06 eV¹¹. More recent experiments have modified the value to 1.53 ± 0.06 eV¹⁰. The computed value for D_0 is 1.65 eV, 0.12 eV larger than experiment. The computed bond distance is 0.017 Å shorter than the experimental value. More interesting is $\Delta G_{1/2}$. Earlier calculations have consistently obtained values that are about 100 cm^{-1} too large. The present result is somewhat low but the error is reduced to 39 cm^{-1} . The improvement is most likely due to the increased active space.

Casey and Leopold performed in 1993 negative ion photoelectron spectroscopic measurements on Cr_2^- and were able to identify a number of vibrational levels for Cr_2 ²¹. The first nine of them could be assigned with certainty and with an accuracy of 10–20 cm^{-1} . The assignment of higher levels was more uncertain and was finally based on the fitted RKR potential. We present in Table II the computed and experimental levels up to $v = 39$.

The RKR potential, deduced from the experimental vibrational frequencies is included in Fig. 1. The difference between this “experimental” and the CPC corrected CASPT2 potential is so small that it cannot be seen in the figure for distances up to 2.7 Å, which is in the middle of the plateau region. Here they start to deviate from each other. The RKR potential continues with the small slope until about 3.0 Å where it, rather suddenly, starts

TABLE I
Spectroscopic constants for Cr_2 obtained from the CASPT2 energies with and without counterpoise corrections (CPC)

Parameter	No CPC	With CPC	Experimental
R_e , Å	1.636	1.662	1.679 ^a
D_0 , eV	1.727	1.647	1.53 ± 0.06 ^b
$\Delta G_{1/2}$, cm^{-1}	427	413	452 ^c

^a From ref.²²; ^b from ref.¹⁰; ^c from ref.²¹

to rise and regains the slope of the theoretical potential. The strong curvature at 3.0 Å is unphysical and is probably not correct. The $\Delta G_{v+1/2}$ values for the first ten frequencies differ from experiment (Table II) by at most 36 cm⁻¹ and this difference decreases with increasing quantum number. For higher frequencies (above $v = 26$) are the theoretical values between 10 and 30 cm⁻¹ too large. The experimental frequencies, however, have an uncertainty of 15–20 cm⁻¹. If we assume an average error of about +10 cm⁻¹ for $\Delta G_{v+1/2}$ in the region $v = 10$ –25, we arrive at an estimated value of 4230 cm⁻¹ for the vibrational frequency for $v = 18$, 4620 cm⁻¹ for $v = 21$, and 5000 cm⁻¹ for $v = 24$. The assignments made by Casey and Leopold give

TABLE II
Calculated (CASPT2 with counterpoise corrections) and experimental vibrational frequencies for Cr₂. Energies in cm⁻¹. Experimental values in parentheses^a

v	$\Delta G_{v+1/2}$	$G(v)-G(0)$	v	$\Delta G_{v+1/2}$	$G(v)-G(0)$
1	413(452)	413(452)	21	142(-)	4862(4570)
2	439(423)	852(875)	22	143(-)	5005(-)
3	428(405)	1279(1280)	23	144(-)	5148(-)
4	401(365)	1681(1645)	24	144(-)	5293(4880)
5	370(340)	2050(1985)	25	145(120)	5438(5000)
6	335(315)	2385(2300)	26	146(115)	5583(5115)
7	298(280)	2683(2580)	27	146(125)	5729(5240)
8	259(250)	2942(2830)	28	146(120)	5875(5360)
9	218(210)	3160(3040)	29	147(130)	6022(5490)
10	180(-)	3339(-)	30	147(125)	6169(5615)
11	150(-)	3490(-)	31	147(130)	6316(5745)
12	137(-)	3627(-)	32	147(125)	6463(5870)
13	134(-)	3761(-)	33	147(130)	6609(6000)
14	134(-)	3895(-)	34	147(135)	6756(6135)
15	135(-)	4029(-)	35	146(130)	6902(6265)
16	136(-)	4165(-)	36	146(135)	7048(6400)
17	137(-)	4302(-)	37	145(130)	7193(6530)
18	138(-)	4440(4290)	38	145(130)	7337(6660)
19	140(-)	4580(-)	39	144(130)	7481(6790)
20	141(-)	4720(-)			

^a From ref.²¹

4290, 4570, and 4880 cm^{-1} , respectively. The first two fit reasonably well with the estimated values. The third is somewhat low but the data are not precise enough to draw any definite conclusions concerning the assignment. Both $\nu = 23$ and 24 are possible. A reassignment might improve the agreement between the theoretical and experimental potentials. If the present experimental curve is essentially correct, one would have to explain the too weak bonding in the outer part of the curve, which is not easy considering that the two curves are parallel. Also, the shape of the experimental potential around 3 Å is unlikely to be correct. The 4s orbital is large and will certainly give rise to a potential that varies more smoothly. It would be very interesting to see an experiment where also the missing frequencies ($\nu = 10\text{--}23$) are measured.

The Core and Valence Correlation Contributions to the Bond Energy

How important is the core-core and core-valence contributions to the binding energy? It is possible to approximately partition the CASPT2 energy into three contributions depending on the type of electron excited. This partitioning is not exact due to coupling elements in the Hamiltonian, but this coupling is small, so an analysis is still meaningful. We show in Fig. 2 how the correlation energy varies with distance.

We notice that the core-core part of the correlation energy goes through a small minimum located at $R = 2.22$ Å and 0.12 eV deep. Further, this part

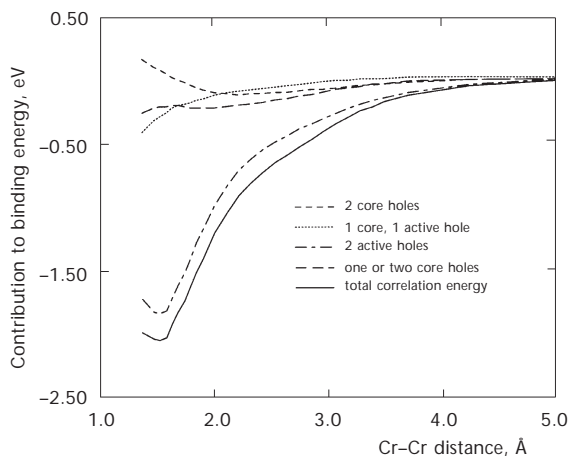


FIG. 2

The variation of the dynamic correlation energy as a function of the interatomic distance in Cr_2

of the correlation energy increases with decreasing distance and the contribution to the binding energy is close to zero. The core valence part, on the other hand, decreases with decreasing distance and has reached the value -0.20 eV at equilibrium. This is thus the total contribution from the core electrons to the binding energy. The contribution to the binding energy from the active (valence) electrons is of course large, 1.61 eV. We notice that it passes through a minimum at 1.52 Å.

CONCLUSIONS

We have presented results of a new calculation of the ground state potential curve for Cr_2 . A new basis set has been constructed that includes scalar relativistic effects and 3s,3p correlation effects. An active space of 16 orbitals was used in the CASSCF and CASPT2 calculations. They include, in addition to the 3d,4s orbitals, four orbitals of mainly 4p character. The resulting potential agrees well with the RKR potential in the 3d bonding region but deviates somewhat in the outer part of the 4s bonding region. It is not clear at the moment how much of this is due to deficiencies in the RKR potential and how much is due to inadequacies in the theoretical treatment. A more complete experimental study of the vibrational frequency for this model molecule would be of great interest.

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