Binding Energy of Chromium Hexacarbonyl. 2. Revisited with Correlation Effects

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The binding energy of Cr(CO)$_6$ was investigated using correlated methods. The multireference CI and QDVARPT approaches yield estimates of the binding energy which are about 72% and 90% of the experimental value. The radial correlation between electrons in the $5\sigma e_g$, $3d*e_g$, $3dt_{2g}$, and $2\pi*t_{2g}$ orbitals is the predominant source of the correlation correction to the bonding.

I. Introduction

A detailed understanding of the bonding between transition-metal carbonyl complexes has been receiving special attention, both theoretically and experimentally, because of their importance in organometallic chemistry and in catalytic processes.[1-2] As is well known, the examination of the binding in transition metal-ligand via ab initio techniques is a difficult task since there are conceptual and practical problems (see ref 3 and references therein).

In a recent paper, Kunze and Davidson (part 1)[4] studied the bonding in Cr(CO)$_6$ in the Hartree–Fock (RHF) approximation. Although this approximation gave some insight into the charge rearrangement that leads to bonding, the RHF model actually predicts that the molecule is unbound. The bond dissociation energy, D_e, of Cr(CO)$_6$, for our purposes, is defined as the energy of the process

$$Cr(CO)_6 \text{ (eq)} \xrightarrow{D_e} Cr(^7S) + 6CO \text{ (eq)} \tag{1}$$
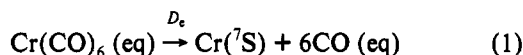
where eq indicates the energy is to be evaluated at the experimental equilibrium configuration. This D_e is a difference in energy between points on two different potential energy surfaces since Cr(CO)$_6$ has octahedral symmetry and a ^1A_g ground state. When spin–orbit coupling is neglected, each potential surface can be labeled by total spin so the $S = 0$ surface for the molecule cannot connect to the $S = 3$ state of the Cr atom. The experimental value for D_e is about 162 kcal/mol.[5-7] In part 1, the RHF model gave –111 kcal/mol; that is, it predicted that the molecule was unbound.

For computational purposes, it is useful to evaluate D_e by carrying out the dissociation in several steps. For step 1, consider

$$Cr(CO)_6 \text{ (eq)} \xrightarrow{D_1} Cr(^1A_g) + 6CO \text{ (cp)} \tag{2}$$
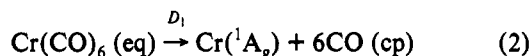
The ^1A_g state of the Cr atom is a hypothetical state having O_h symmetry and the electron configuration t_{2g}^6 characteristic of the atom in the complex. The CO (cp) energy is the energy of CO at the bond length in the complex. These promoted fragments can be formed by

$$Cr(^7S) \xrightarrow{P_{Cr}} Cr(^1A_g) \tag{3}$$

and

$$CO \text{ (eq)} \xrightarrow{P_{CO}} CO \text{ (cp)} \tag{4}$$
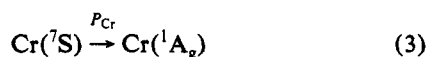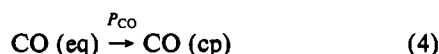
where P_{Cr} is the promotion energy for Cr and P_{CO} is the promotion

energy for one carbonyl. These energies are related by

$$D_e = D_1 - P_{Cr} - 6P_{CO} \tag{5}$$

In part 1, an older value for the CO bond length in the complex was used.[8] This led to P_{CO} being about 6 kcal/mol in the RHF approximation. It was pointed out in part 1 that using the more recent experimental structure[9,10] would reduce P_{CO} to only 1 kcal/mol. As shown in the present paper, this has little effect on D_1, so the calculated RHF value of D_e is improved by 30 kcal/mol by using this improved bond length.

This bond length change still leaves the molecule unbound by about 80 kcal/mol in the RHF model. In part 1, guesses were made of the effect of electron correlation on D_1, P_{Cr}, and P_{CO}. In the present study, these electron correlation effects are evaluated using MP2 and configuration interaction approaches.

A problem with calculations in molecules using limited basis sets is that the orbitals of one fragment in the complex tend to complete the basis sets of other fragments. Thus, the energy of each fragment calculated in the full basis set of the complex may be substantially lower than when calculated in its own basis. This will appear as an artificial stabilization of the complex that is really just due to an improved description of each monomer. One method of estimating the magnitude of this effect, known as the basis set superposition error (BSSE), is to calculate the energy of each monomer in the full molecular basis. This method is called the counterpoise correction.[11] It is especially important to make this correction for inorganic complexes because it also corrects a common misconception in the inorganic literature. It is often claimed, for example, that Cr(CO)$_6$ is stabilized by HOMO–LUMO mixing of the 3d occupied orbitals of Cr and the empty $\pi*$ orbitals of CO. While this is true in some sense, it is important that just adding the $\pi*$ orbitals of CO (without adding the CO molecules) should not change the energy of the Cr atom. In part 1, a basis set was developed that had very little BSSE in the RHF energy. In this paper, we examine the BSSE effect on the electron correlation.

Another source of error in calculations is size inconsistency. Some methods of evaluating the energy give a different result for the assembly of Cr and 6CO treated as a "supermolecule" consisting of fragments well separated from each other than for the sum of the energies of each fragment evaluated separately. In such methods, the energy of the complex is most comparable to the supermolecule energy, so D_1 should be evaluated using the supermolecule result. The RHF energy is size-consistent; i.e., it has no size-inconsistency error. Configuration interaction is generally not size-consistent. The MP2 method is preferred for the electron correlation problem because it is normally size-consistent. In the present study, we have introduced further approximations that cause even MP2 to be somewhat size-inconsistent.

The remainder of the paper is organized as follows. In section II, the geometry and basis set which were used are discussed

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along with the wave functions employed. In section III, the results are presented and discussed. Section IV contains concluding remarks.

II. Methodology

The basis set used in this study is the same as the basis set in part 1.[4] As shown in the supplementary material from part 1, this basis set gives an energy which is 4 kcal/mol above the SCF limit for CO and 0.2 kcal/mol above the SCF limit for Cr. From calculations on each fragment in the full $Cr(CO)_6$ basis, the total RHF basis set superposition error was estimated to be 7 kcal/mol.

In part 1 the geometry of $Cr(CO)_6$ used was the crystal structure obtained by Whitaker and Jeffrey[8] with a Cr–C bond length of 1.916 Å, a CO bond length of 1.171 Å, and a linear Cr–C–O bond angle. In that paper they found that this geometry leads to an energy somewhat too large to stretch CO. In the calculations reported here, we have used a CO bond length of 1.140 Å as obtained by Jost et al.[9] from low-temperature neutron diffraction and confirmed by Rees and Mitschler,[10] who have combined low-temperature X-ray data with neutron diffraction. The calculations were done with atoms in O_h symmetry positions, but only D_{2h} symmetry imposed on the orbitals.

Electron correlation was studied using the second-order Møller–Plesset perturbation theory (MP2),[12,13] configuration interaction (CI), quasidegenerate variational perturbation theory (QD-VARPT),[14] and linearized coupled cluster (LCC).[15] All these methods are implemented in the MELD suite of electronic structure codes developed in this laboratory.[16]

The importance to the binding energy of correlating all valence electrons has been shown by Blomberg et al.[17,18] for $Ni(CO)_x$ (x = 1–4). Also, 3s3p correlation is known to be important to the atom term separation for the transition metal,[19] and we have noted that there is a significant overlap between the CO 5σ orbital and the 3s and 3p orbitals of Cr. In order to investigate the importance of correlating all valence electrons plus the 3s3p electrons on Cr to the binding energy of $Cr(CO)_6$, we have carried out some MP2 calculations. In these calculations, we have correlated six, eight, and ten electrons on CO and six and fourteen electrons on Cr. In the calculations correlating ten electrons on CO and six electrons on Cr the last molecular orbitals in the symmetries a_g, b_{1u}, b_{2u}, and b_{3u} were considered inactive. Also, the last two orbitals in these symmetries were considered inactive when eight and ten electrons on CO and fourteen electrons on Cr were correlated. It should be evident that we have broken the size consistency of the method by these restrictions. However, we could make an estimation of the contribution from the correlation of these electrons to the binding energy.

The CI, QDVARPT, and LCC calculations were carried out correlating all ten valence electrons on CO. The wave functions were computed using the perturbation-theory-selected multireference single and double excitations (MRSD). The multireference configurations were chosen from a preliminary Hartree–Fock single and double configuration interaction (HFSD-CI) calculation with coefficient contributions of at least 0.05. The configurations chosen represent all double excitations from the Cr $3d(t_{2g})$ orbital to the Cr $3d^*(t_{2g})$ orbital. Therefore, the calculation on each fragment was done using the multireference configurations that represent the same kind of excitation. In these calculations the molecular orbitals (MO's) used in the expansion of the wave functions were the K orbitals.[20] For MP2 calculations the MO's were the canonical orbitals as described in ref 12.

All the values reported for the bonding energy using the CI, QDVARPT, and LCC calculations were taken from the extrapolation procedure.[21] As shown by Antolovic and Davidson,[22] the extrapolation results provide a degree of size consistency, which is necessary for a meaningful comparison of the CI energy

TABLE I: Promotion Energy for the Chromium Atom[a]

method	$E(^7S)$	$E(^5S)$	$E(^1A_g)$	$^1A_g-^7S$
SCF	-1043.355 92		-1042.986 47	232
MP2 (6 e)[b]	-1043.430 55		-1043.154 62	173
MP2 (14 e)[b]	-1043.664 31		-1043.403 08	164
MRSDCI (6 e)[b,c]		-1043.399 86	-1043.144 84	182
MRSDCI (6 e)[b-d]		-1043.404 1	-1043.14 86	182
MRSDCI (14 e)[b,c]		-1043.583 66	-1043.360 73	162
MRSDCI (14 e)[b-d]		-1043.602 3	-1043.382 3	160
QDVARPT (6 e)[b,c]		-1043.404 39	-1043.149 12	182
QDVARPT (6 e)[b-d]		-1043.404 59	-1043.149 43	182
QDVARPT (14 e)[b,c]		-1043.604 58	-1043.385 62	159
QDVARPT (14 e)[b-d]		-1043.605 29	-1043.386 84	159

[a] Energies in hartrees. Separation energies in kilocarlories per mole. [b] Number of electrons correlated. [c] The energy of ^7S is calculated from the ^5S energy plus the experimental separation energy equal to 0.0346 au (21.7 kcal/mol).[23] [d] Results from the extrapolation procedure.[21]

TABLE II: Basis Set Superposition Errors for Some $Cr(CO)_6$ Fragments (kcal/mol)

	SCF	MP2 (6 e)[a]	MP2 (8 e)[a]	MP2 (10 e)[a]
Cr(ghost) + CO	0.58	1.27	1.61	1.95
CO(ghost) + CO	0.005	0.027	0.046	0.103
CO_p(ghost) + CO[b]	0.087	0.178	0.247	0.316
Cr + $(CO)_6$(ghost)	0.41	4.8	4.8	4.8
Cr + $(CO)_6$(ghost)(3s3p)[c]	0.41	12.9	12.9	12.9
total 1[d]	6.01	16.85	20.66	24.70
total 2[e]	6.01	24.95	28.76	32.80

[a] The number of electrons correlated in CO. [b] CO perpendicular to the other CO. [c] The 3s and 3p electrons in Cr are also correlated. [d] Total 1 = 6[(Cr(ghost) + CO) + (CO(ghost) + CO) + 4(CO_p(ghost) + CO)] + [Cr + $(CO)_6$(ghost)]. [e] Total 2 = 6[(Cr(ghost) + CO) + (CO(ghost) + CO) + 4(CO_p(ghost) + CO)] + [Cr(3s3p) + $(CO)_6$(ghost)].

TABLE III: Hartree–Fock Results

	energy (au)	D (kcal/mol)	D(BSSE) (kcal/mol)
$Cr(CO)_6$	-1719.912 50		
CO($^1\Sigma^+$)[a]	-112.781 04		
CO($^1\Sigma^+$)[b]	-112.779 32		
Cr(^7S)[c]	-1043.355 92	-81	-87
Cr(^1A_g)[d]	-1042.986 47	157	144

[a] r(CO) = experimental bond length for free CO = 1.1283 Å. [b] r(CO) = bond length for CO in the complex = 1.140 Å. [c] The D_e value relative to CO (eq). [d] The D_1 values relative to CO stretched.

of the complex with that of the products of dissociation. Also, they showed that the extrapolation energy is nearly independent of the size of the CI matrix.

For the chromium atom the correlated calculations were carried out on the states of symmetry ^7S, ^5S ($4s^13d^5$), and hypothetical ^1A_g (d^6). The orbitals used in the expansion of the wave functions were obtained in high spin symmetry. Due to spin symmetry limitations in the MELD codes, the energies reported for CI, QDVARPT, and LCC calculations to the ground state ^7S ($4s^1$-$3d^5$) were obtained from the results of ^5S plus the experimental[23] ^5S–^7S separation energy equal to 0.94 eV (21.7 kcal/mol). The MP2 calculations for ^7S were made using the Gaussian 92 program.[24]

III. Results and Discussion

A. Atomic Promotion Energy of Chromium. Table I presents the promotion energy results of Cr relative to ^1A_g–^7S calculated using RHF, MP2, and multireference CI and QDVARPT approaches. The multireference configurations used in the multireference calculations consist of all the double excitations from the Cr $3d(t_{2g})$ orbital to Cr $3d^*(t_{2g})$ orbital.

As is known, the RHF wave function for the complex is best described as t_{2g}^6 ^1A_g Cr complexed to carbonyls in their ground state. Thus, it is important to know the promotion energy to

TABLE IV: MP2 Results[a,b]

	CO(6 e) Cr(6 e)[c]	CO(8 e) Cr(6 e)[c]	CO(10 e) Cr(6 e)[c]	CO(6 e) Cr(14 e)[c]	CO(8 e) Cr(14 e)[c]	CO(10 e) Cr(14 e)[c]
			D			
$Cr(CO)_6$	−1721.298 04	−1721.826 66	−1722.206 41	−1721.570 02	−1722.100 67	−1722.479 65
D_e, $Cr(^7S)^d$	185 (168)	194 (173)	204 (179)	209 (184)	225 (196)	235 (202)
D_1, $Cr(^1A_g)^e$	360 (343)	368 (347)	372 (347)	375 (350)	384 (355)	388 (355)
D_1, supermol^f	360 (343)	368 (347)	376 (351)	375 (350)	389 (360)	398 (365)

^{a} $Cr(CO)_6$ energies are in hartrees. Dissociation energies are in kilocalories per mole. ^{b} Values in parentheses are corrected for BSSE. ^{c} The number of electrons correlated. The CO energies with six, eight, and two electrons correlated are, respectively, −112.928 70, −113.014 37, and −113.076 21. ^{d} D_e results computed as $D_1 - P_{Cr} - 6P_{CO}$ using D_1 from the supermolecule. The $Cr(^7S)$ energy with fourteen electrons correlated is −1043.664 31 hartrees. The $Cr(^7S)$ energy with six electrons correlated is −1043.430 55 hartrees. ^{e} The $Cr(^1A_g)$ energy with six electrons correlated is −1043.154 62 hartrees. The $Cr(^1A_g)$ energy with fourteen electrons correlated is −1043.403 08 hartrees. Results with CO stretched. The energies with six, eight, and ten electrons correlated are, respectively, −112.928 24, −113.014 34, and −113.076 49. D_1 calculated relative to the sum of fragment energies. ^{f} D_1 results relative to the supermolecule [r(M–C) = 103.62072a_0, r(CO) = 2.15429a_0].

prepare this hypothetical state. In part 1, Kunze and Davidson estimated the promotion energy to be around 150 kcal/mol. Since the RHF result is equal to 232 kcal/mol, the contribution of the correlation correction is expected to be −82 kcal/mol.

From these results we conclude that the 3s3p correlation is important to describe the chromium atom in the hypothetical state. The difference in the promotion energy when six or fourteen electrons are correlated is 9 kcal/mol at the MP2 level. In the multireference methods, this difference goes to 20 kcal/mol. The inclusion of the inner core electron's correlation does not change the promotion energy result at the MP2 level. However, the MRSD-CI and QDVARPT methods yield values of 157 and 156 kcal/mol, respectively. Hence, we conclude that the estimation of 150–160 kcal/mol is a very good value.

B. Basis Set Superposition Error (BSSE). The BSSE was estimated using the counterpoise method[11] for the SCF and MP2 approaches. The results are given in Table II. The BSSE was estimated for the chromium atom in the ^1A_g state and for the CO molecule in the stretched geometry.

In these calculations, the estimation of the BSSE for the ^1A_g chromium atom was obtained using all CO basis functions. The contribution for one CO was taken from the sum of the BSSE when the chromium and each of the five CO bases were included. Thus, the total BSSE estimation at the Hartree–Fock level is 6.0 kcal/mol for assembling the complex from the fragments.

At the MP2 level, the estimation of BSSE was carried out correlating six or fourteen electrons on Cr, and correlating six, eight, or ten electrons on CO. The last six orbitals in symmetry a_g, the last two orbitals in symmetries b_{1u}, b_{2u}, and b_{3u}, and the last orbital in symmetries b_{1g}, b_{2g}, b_{3g}, and a_u were considered inactive. In the calculations on the Cr atom which correlated fourteen electrons, one more orbital in the symmetries a_g, b_{1u}, b_{2u}, and b_{3u} was also considered inactive. Since the BSSE on the chromium atom is expected to be small, this truncation on orbital space leads to an error of no more than 1 kcal/mol. Hence, the total estimated BSSE was 24.7 kcal/mol when all valence electrons were correlated and 32.8 kcal/mol when 3s3p electrons on chromium were also correlated. These results can be compared with the recent results obtained from Barnes et al.,[5] which used the modified coupled-pair functional (MCPF) method. Their basis gave 21.9 and 22.6 kcal/mol, respectively, for these same superposition errors. However, it should be noted that their estimations were carried out relative to the Cr in the ^7S state and to CO in the $(CO)_6$ cage.

C. Hartree–Fock Results. In Table III, the Hartree–Fock results are presented for the total energies and for the dissociation energies relative to the ground ^7S state (D_e), and to the ^1A_g state of chromium (D_1) plus six CO molecules. The RHF dissociation energies calculated from the supermolecule and calculated from the sum of the fragments with the chromium atom in a hypothetical t_{2g}^6 ^1A_g state are equal, as expected. Although we have used a better CO bond length than the one used in part 1, we still found

TABLE V: Single Reference Results

	CI		QDVARPT	
	energy	D	energy	D
$Cr(CO)_6$	−1722.2231		−1722.331 51	
CO	−113.0894		−113.091 41	
$Cr(^5S)$	−1043.6008		−1043.604 14	
$Cr(^7S)^{a,b}$	−1043.6354	32 (97)	−1043.638 74	91 (103)
$Cr(^1A_g)$	−1043.3791		−1043.389 86	
$Cr(^1A_g)^{a,c}$	−1043.3791	192 (257)	−1043.389 86	246 (258)
supermol^d	−1721.8133		−1721.919 78	

^{a} Values in parentheses are corrected for estimation of the size consistency error (see text) by adding E(supermolecule) − E(promoted fragments). Total energies are in hartrees, and D is in kilocalories per mole. ^{b} The energy is calculated from the ^5S energy plus the experimental ^5S–^7S separation energy equal to 0.0346 au (21.7 kcal/mol) to give D_e. ^{c} Results with CO stretched to give D_1. ^{d} Supermolecule]r(M–C) = 103.62072a_0, r(CO) = 2.15429a_0].

the molecule to be unbound by 87 kcal/mol (compared to 111 kcal/mol in part 1) relative to ground-state fragments. This improvement in the bond energy of 24 kcal/mol is a consequence of a better description for the CO stretching promotion. Hence, the RHF fragment promotion energy, $P_{Cr} + 6P_{CO}$, is 239 kcal/mol (compared to 266 kcal/mol in part 1) for preparing six stretched CO molecules and a t_{2g}^6 ^1A_g chromium atom.

D. MP2 Results. The results obtained from MP2 calculations with six and fourteen electrons correlated on Cr and with six, eight, and ten electrons correlated on the CO molecule are presented in Table IV. The corrections due to truncations in orbital space, when all valence electrons were correlated and when fourteen electrons on Cr and eight and ten electrons on CO were correlated, are also estimated assuming that the contributions are equal to the complex and to the fragments with Cr in the ^1A_g and ^7S states.

First, it is important to discuss the results of the free CO calculations. As is well known, MP2 gives a bond length larger than the experimental one. Using the 6-31G* basis set, it is 2.175a_0.[25] The experimental value is 2.1322a_0.[26] Using our basis set and correlating ten valence electrons, the MP2 bond length of free CO is equal to 2.154a_0, which is, by chance, exactly the experimental stretched value in the complex. The calculated difference in the energy between the experimental equilibrium and stretched distances of six CO is 2–1 kcal/mol depending on how many electrons are correlated. Therefore, this difference, $6P_{CO}$, does not have a great effect on the binding energy.

All the MP2 results overestimate the correlation correction to the binding energy even when including the BSSE correction. However, the results show that it is important to correlate all valence electrons on CO as was obtained before for $Ni(CO)_x$ (x = 1–4).[17,18] The importance of correlating 3s3p electrons on Cr, as discussed before, plays a special role for the promotion energy. The binding energy overestimation is 17 kcal/mol when all valence electrons are correlated. The inclusion of 3s3p correlation on Cr improves the promotion energy by 9 kcal/mol. However, it increases the overestimation in the correlation correction by 14

TABLE VI: Multireference Results

	CI		QDVARPT		MRLCC	
	energy	D	energy	D	energy	D
$Cr(CO)_6$	-1722.2389		-1722.369 14		-1722.289 31	
CO	-113.0894		-113.091 41		-113.091 41	
$Cr(^5S)^a$	-1043.6021		-1043.605 08		-1043.604 10	
$Cr(^7S)^{a,b}$	-1043.6367	41 (117)	-1043.639 68	114 (146)	-1043.638 70	64 (98)
$Cr(^1A_g)^a$	-1043.3813		-1043.384 79		-1043.384 08	
$Cr(^1A_g)^{a,c}$	-1043.3813	201 (277)	-1043.384 79	272 (304)	-1043.384 08	223 (257)
supermol^d	-1721.7981		-1721.884 12		-1721.879 12	

[a] Values in parentheses are corrected for estimation of the size consistency error (see text) by adding E(supermolecule) $-$ E(promoted fragments). Total energies are in hartrees, and D is in kilocalories per mole. [b] The energy is calculated from the ^5S energy plus the experimental ^5S–^7S separation energy equal to 0.0346 au (21.7 kcal/mol) to give D_e. [c] Results with CO stretched to give D_1. [d] Supermolecule [r(M–C) = $103.62072a_0$, r(CO) = $2.15429a_0$].

TABLE VII: Previously Correlated Binding Energy Calculations for $Cr(CO)_6$

method	year	D_e (kcal/mol)	method	year	D_e (kcal/mol)
experimental^a	1975	162	SDCI	1993	97
SDCI^b	1983	200	LCC	1993	103
MCPF^c	1991	109.5	MRSD-CI	1993	117
MCPF^d	1993	117.1	QDVARPT	1993	146
CCSD(T)^e	1993	139.4	MRLCC	1993	98
this work^f			MP2	1993	235

[a] See text, refs 5–7. [b] Reference 27. [c] Reference 28. [d] Reference 5. Results including 3s3p correlation. [e] Reference 5. Results wihotu 3s3p correlation. [f] Relative to the supermolecule energy to get D_1 and fragment calculations to get P_{Cr} and P_{CO} without BSSE correction.

TABLE VIII: Contribution of the Main Configurations in the Complex CI Wave Functions

	configuration	orbitals involved	coef
1	det_{HF}		-0.8758
2	$^1(3b_{2g} 4b_{2g})^1(3b_{3g} 4b_{3g})$	$^1(3dt_{2g} 2\pi^*t_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0620
2a	$^1(3b_{2g} 4b_{3g})^1(3b_{3g} 4b_{2g})$	$^1(3dt_{2g} 2\pi t^*_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0093
3	$^1(3b_{1g} 4b_{1g})^1(3b_{3g} 4b_{3g})$	$^1(3dt_{2g} 2\pi^*t_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	0.0620
3a	$^1(3b_{1g} 4b_{3g})^1(3b_{3g} 4b_{1g})$	$^1(3dt_{2g} 2\pi^*t_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	0.0093
4	$^1(3b_{1g} 4b_{1g})^1(3b_{2g} 4b_{2g})$	$^1(3dt_{2g} 2\pi^*t_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0620
4a	$^1(3b_{1g} 4b_{2g})^1(3b_{2g} 4b_{1g})$	$^1(3dt_{2g} 2\pi^*t_{2g})^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0093
5	$3b_{3g}^2 \rightarrow 4b_{3g}^2$	$3dt_{2g}^2 \rightarrow 2\pi^*t_{2g}^2$	0.0431
6	$3b_{1g}^2 \rightarrow 4b_{1g}^2$	$3dt_{2g}^2 \rightarrow 2\pi^*t_{2g}^2$	0.0431
7	$3b_{2g}^2 \rightarrow 4b_{2g}^2$	$3dt_{2g}^2 \rightarrow 2\pi^*t_{2g}^2$	0.0431
8	$^1(18a_g 19a_g)^1(3b_{3g} 4b_{3g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	0.0342
8a	$^1(18a_g 4b_{3g})^1(3b_{3g} 19a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	-0.0037
9	$^1(17a_g 20a_g)^1(3b_{1g} 4b_{1g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0323
9a	$^1(17a_g 4b_{1g})^1(3b_{1g} 20a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	0.0038
10	$^1(17a_g 20a_g)^1(3b_{2g} 4b_{2g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	0.0321
10a	$^1(17a_g 4b_{2g})^1(3b_{2g} 20a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	-0.0038
11	$^1(18a_g 19a_g)^1(3b_{2g} 4b_{2g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0284
11a	$^1(18a_g 4b_{2g})^1(3b_{2g} 19a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	0.0039
12	$^1(18a_g 19a_g)^1(3b_{1g} 4b_{1g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	0.0282
12a	$^1(18a_g 4b_{1g})^1(3b_{1g} 19a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	-0.0039
13	$^1(17a_g 20a_g)^1(3b_{3g} 4b_{3g})$	$^1(5\sigma e_g 3d^*e_g)^1(3dt_{2g} 2\pi^*t_{2g})$	-0.0258
13a	$^1(17a_g 4b_{3g})^1(3b_{3g} 20a_g)$	$^1(5\sigma e_g 2\pi^*t_{2g})^1(3dt_{2g} 3d^*e_g)$	0.0038

kcal/mol. Hence, an overestimation of the binding energy equal to 40 kcal/mol resulted when all valence plus 3s3p electrons were correlated. These results were estimated relative to the D_e value equal to 162 kcal/mol[5] which was obtained from the experimental value of D_0 = 154 kcal/mol[6] and from the data of the zero point energy reported by Pilcher et al.[7]

From the RHF energies and the experimental binding energy, the change in correlation energy upon forming the molecule from ^7S chromium and six CO molecules is known to be 249 kcal/mol. The total correlation energy when fourteen electrons of chromium and ten electrons of each CO are correlated is expected to be about 1800 kcal/mol so the change in correlation energy is only 13% of the total. The basis set used here gives about 1500 kcal/mol or 80% of the correlation energy. Clearly the method for describing the correlation energy must be carefully chosen so that the change in correlation energy can be estimated accurately from the difference of two inaccurate calculations.

TABLE IX: Contribution of the Main Configurations in the Supermolecule CI Wave Functions

	configuration	orbitals involved	coef
1	det_{HF}		0.8751
2	$^1(3b_{2g} 4b_{2g})^1(3b_{3g} 4b_{3g})$	$^1(3dt_{2g} 3d^*t_{2g})^1(3dt_{2g} 3d^*t_{2g})$	0.0583
2a	$^1(3b_{2g} 4b_{3g})^1(3b_{3g} 4b_{2g})$	$^1(3dt_{2g} 3dt^*_{2g})^1(3dt_{2g} 3d^*t_{2g})$	0.0100
3	$^1(3b_{1g} 4b_{1g})^1(3b_{3g} 4b_{3g})$	$^1(3dt_{2g} 3d^*t_{2g})^1(3dt_{2g} 3d^*t_{2g})$	0.0583
3a	$^1(3b_{1g} 4b_{3g})^1(3b_{3g} 4b_{1g})$	$^1(3dt_{2g} 3d^*t_{2g})^1(3dt_{2g} 3d^*t_{2g})$	0.0100
4	$^1(3b_{1g} 4b_{1g})^1(3b_{2g} 4b_{2g})$	$^1(3dt_{2g} 3d^*t_{2g})^1(3dt_{2g} 3d^*t_{2g})$	-0.0583
4a	$^1(3b_{1g} 4b_{2g})^1(3b_{2g} 4b_{1g})$	$^1(3dt_{2g} 3d^*t_{2g})^1(3dt_{2g} 3d^*t_{2g})$	-0.0100
5	$^1(8b_{3u} 12b_{3u})^1(2b_{1g} 5b_{1g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0367
5a	$^1(8b_{3u} 5b_{1g})^1(2b_{1g} 12b_{3u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0212
6	$^1(7b_{3u} 13b_{3u})^1(2b_{2g} 5b_{2g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0367
6a	$^1(7b_{3u} 5b_{2g})^1(2b_{2g} 13b_{3u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0212
7	$^1(8b_{2u} 12b_{2u})^1(1b_{1g} 6b_{1g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0367
7a	$^1(8b_{2u} 6b_{1g})^1(1b_{1g} 12b_{2u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0212
8	$^1(8b_{1u} 12b_{1u})^1(1b_{2g} 6b_{2g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0367
8a	$^1(8b_{1u} 6b_{2g})^1(1b_{2g} 12b_{1u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	0.0212
9	$^1(7b_{1u} 13b_{1u})^1(2b_{3g} 5b_{3g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0367
9a	$^1(7b_{1u} 5b_{3g})^1(2b_{3g} 12b_{1u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0212
10	$^1(7b_{2u} 13b_{2u})^1(2b_{3g} 5b_{3g})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0367
10a	$^1(7b_{2u} 5b_{3g})^1(2b_{3g} 13b_{2u})$	$^1(1\pi 2\pi^*)^1(1\pi 2\pi^*)$	-0.0212
11	$3b_{3g}^2 \rightarrow 4b_{3g}^2$	$3dt_{2g}^2 \rightarrow 3d^*t_{2g}^2$	-0.0390
12	$3b_{1g}^2 \rightarrow 4b_{1g}^2$	$3dt_{2g}^2 \rightarrow 3d^*t_{2g}^2$	-0.0390
13	$3b_{2g}^2 \rightarrow 4b_{2g}^2$	$3dt_{2g}^2 \rightarrow 3d^*t_{2g}^2$	-0.0390

E. CI, QDVARPT, and LCC Results. The results of binding energies for $Cr(CO)_6$ using perturbation-selected single reference and multireference methods are presented in Tables V and VI, respectively. The calculations were carried out using the same energy contribution threshold for the complex and for the fragments in the process of perturbation theory selection. All the results reported were from the extrapolation procedure.[21]

It is more reasonable to calculate the dissociation from the supermolecule approach in order to reduce the size consistency error. Assuming this, we then estimated the corrections due to the size consistency error. Using these results, we see that in the single reference calculations the CI and QDVARPT (LCC) methods yield approximately the same binding energies. In the multireference calculations, the QDVARPT results are better than the CI and MRLCC results, by about 27 and 47 kcal/mol, respectively.

Table VII shows a comparison of our results of binding energy with some previous correlated values found in the literature. Most of the calculations were carried out using different Cr–C and C–O bond lengths. All the reported results are without BSSE corrections. As we can see, with the exception of Moncrieff et al.[27] results which overestimated the binding energy, all the results are comparable. However, our QDVARPT value is closer to the experimental value, although Barnes et al.[5] reported one CCSD-(T) result including the 3s3p correlation equal to 125 kcal/mol after BSSE correction.

F. Discussion. The important question not answered by the previous calculations concerns the primary source of bonding. Tables VIII and IX give the most important configurations of the
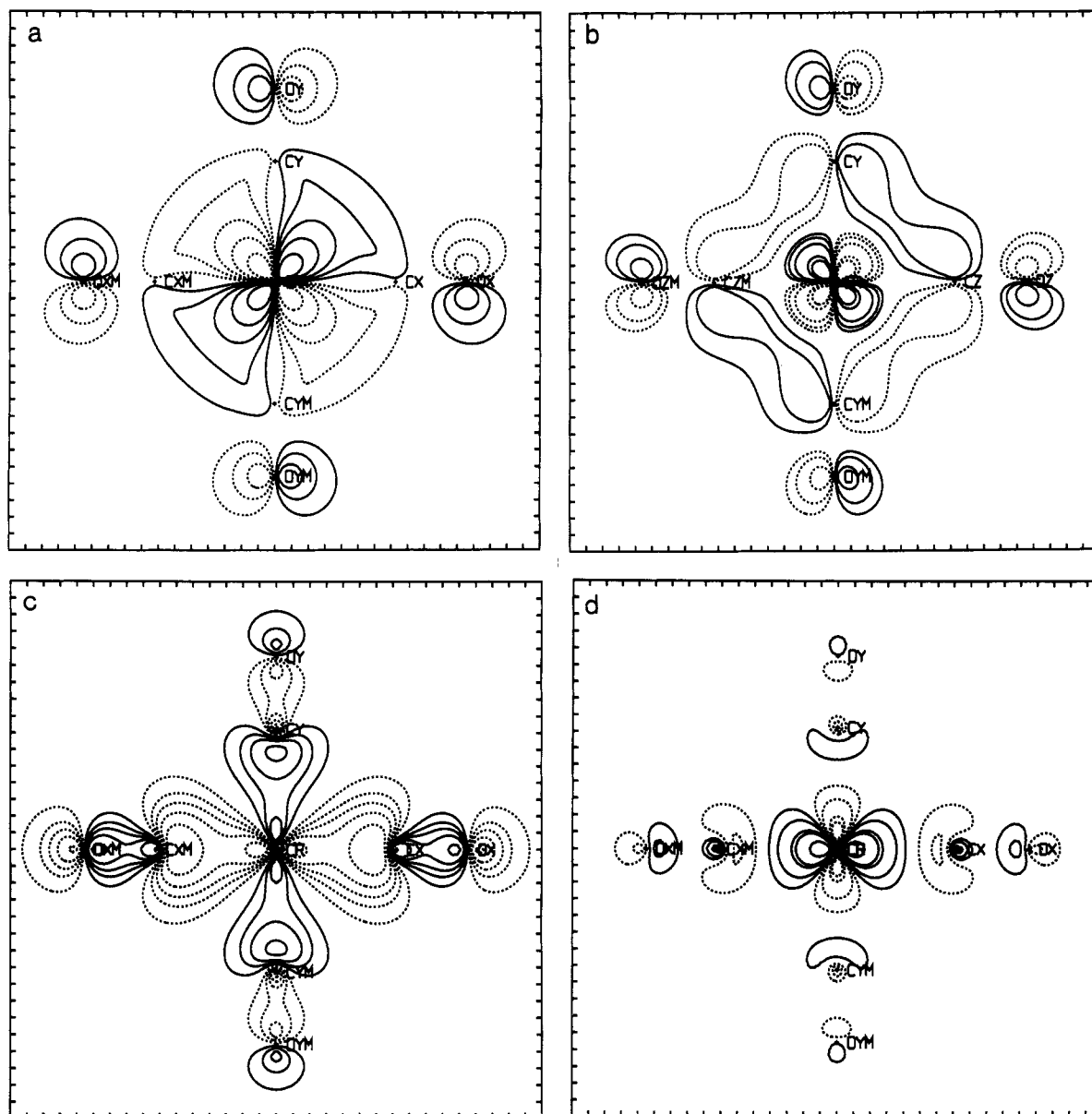
Figure 1. Orbitals in the $Cr(CO)_6$ molecule: (a) $3dt_{2g}$ ($3b_{1g}$, $3b_{2g}$, $3b_{3g}$) orbital; (b) $2\pi^*t_{2g}$ ($4b_{1g}$, $4b_{2g}$, $4b_{3g}$) orbital; (c) $5\sigma e_g$ ($17a_g$, $18a_g$) orbital; (d) $3d^*e_g$ ($19a_g$, $20a_g$) orbital.[29]

complex molecule and of the supermolecule approach, respectively. These are taken from the MRSD-CI calculations based on the K orbitals.

First, notice Figures 1 and 2 which show the orbitals involved. In the complex, the orbital $2t_{2g}$ ($3b_{1g}$, $3b_{2g}$, $3b_{3g}$ in D_{2h} symmetry) could be represented as mostly the $3dt_{2g}$ orbital mixing with the 1π and $2\pi^*$ orbitals of CO. The $3t_{2g}$ ($4b_{1g}$, $4b_{2g}$, $4b_{3g}$) orbital is the antibonding counterpart to $2t_{2g}$ and will be labeled as $2\pi^*t_{2g}$. The $5e_g$ ($17a_g$, $18a_g$) orbital is the $5\sigma e_g$ orbital of CO with some $3de_g$ character. The orbital $6e_g$ ($19a_g$, $20a_g$) is the antibonding combination of $3dt_{2g}$ and $5\sigma e_g$ and will be labeled as $3d^*e_g$.

In the supermolecule, the orbitals ($3b_{1g}$, $3b_{2g}$, $3b_{3g}$) and the orbitals ($4b_{1g}$, $4b_{2g}$, $4b_{3g}$) are the $3dt_{2g}$ and $3d^*t_{2g}$ orbitals, centered on chromium, respectively. The 1π and $2\pi^*$ orbitals centered on each CO give the t_{1u}, t_{2u}, t_{1g}, and t_{2g} combinations of the orbitals $7,8$(b_{1u},b_{2u},b_{3u}) and $1,2$(b_{1g},b_{2g},b_{3g}) and the combinations $12,-13$(b_{1u},b_{2u},b_{3u}) and $5,6$(b_{1g},b_{2g},b_{3g}), respectively. The $3d^*$ orbital is a typical lone pair correlating orbital with the nodal pattern of a $4d$ orbital, but the size of the $3d$ orbital. The other orbitals are familiar valence orbitals.

The dominant configuration in both the complex and supermolecule is the SCF configuration with a coefficient more than 10 times larger than any other configuration. The next group of

configurations in both the complex and supermolecule are $3dt_{2g}$ to $2\pi^*t_{2g}$ or $3d^*t_{2g}$ double excitations. In the supermolecule this represents radial correlation in the $t_{2g}{}^6\,{}^1A_g$ Cr atom that accounts for much of the correlation correction to the promotion energy from ^7S. These double excitations increase the probability that, when one of the excited $3dt_{2g}$ electrons is closer to the nucleus than the radial node in $3d^*t_{2g}$, the other electron will be outside that node and vice versa.

As discussed in part 1,[4] this same correlation effect contributes even more in the complex and hence adds to the stability relative to the ^1A_g asymptote. In the complex both $3d$ and $3d^*$ are more diffuse due to their penetration by the 5σ orbital of CO. These expanded orbitals contain appreciable $2\pi^*$ character. The $3d^*$ correlation orbital, especially, becomes mostly $2\pi^*t_{2g}$.

The next set of correlating configurations in the supermolecule are the many possible double excitations from 1π to $2\pi^*$. These configurations represent left–right correlation of the π electrons in each CO that is awkwardly described by these delocalized symmetry orbitals. In the complex these configurations make a smaller energy contribution, so this type of electron correlation destabilizes the molecule.

In the complex the next most important configurations are the double excitations from $5\sigma e_g$ to $3d^*e_g$ coupled with $3dt_{2g}$ to $2\pi^*t_{2g}$.
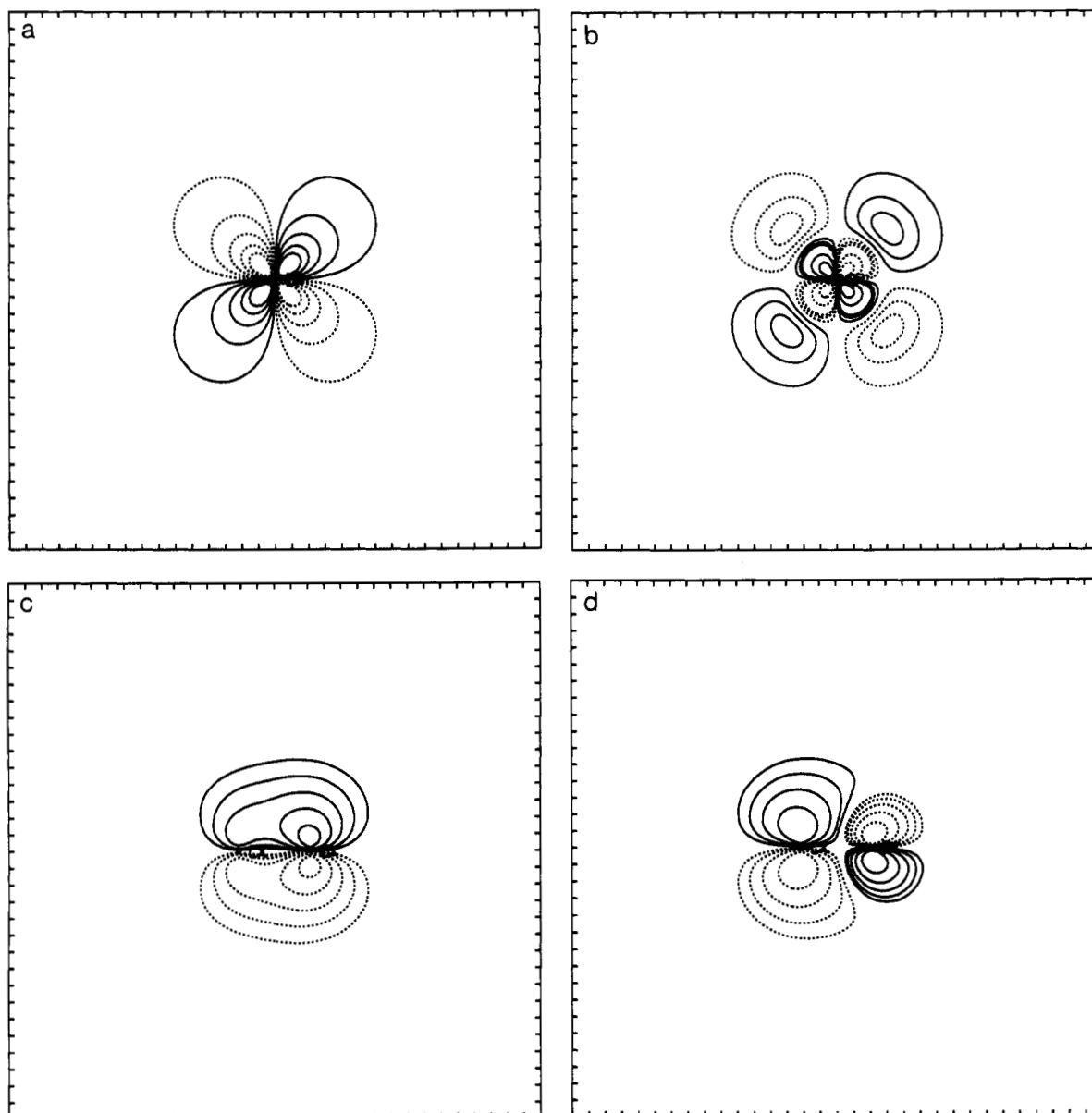
Figure 2. Orbitals in the supermolecule model of $Cr(CO)_6$: (a) $3dt_{2g}$ ($3b_{1g}$, $3b_{2g}$, $3b_{3g}$) orbital; (b) $3d^*t_{2g}$ ($4b_{1g}$, $4b_{2g}$, $4b_{3g}$) orbital; (c) 1π (7,8-(b_{1u},b_{2u},b_{3u}), 1,2(b_{1g},b_{2g},b_{3g})) orbital; (d) $2\pi^*$ (12,13(b_{1u},b_{2u},b_{3u}), 5,6(b_{1g},b_{2g},b_{3g})) orbital.[29]

This double charge transfer configuration makes a contribution that vanishes exponentially with distance as the complex is pulled apart to the supermolecule. It represents a radial correlation between the 5σ and $3d$ electrons so that when the 5σ electron is farther than average from carbon (and hence closer than average to Cr), the $3d$ electrons will compensate by being closer than average to carbon (and hence farther than average from Cr) and vice versa.

In the previous literature most calculations focused on the energy without examining the wave function. The exception was ref 27 that ascribed a large part of the binding energy to the double charge transfer excitation $(3dt_{2g})^2$ to $(2\pi^*)^2$. As noted here, this excitation is, indeed, important, but it persists in the supermolecule and serves primarily to lower the promotion energy of the free chromium atom. The new double charge transfer identified here is interesting because it maintains the SCF charge partitioning while giving an energy contribution that vanishes exponentially with distance.

In part 1,[4] it was assumed that the extra molecular correlation energy would be of the dispersion energy type so it should vanish like a negative power of R. In making Table VII, we have partitioned configurations like number 8 into two nonorthogonal parts. Because this configuration has four singly occupied orbitals,

there are two possible independent ways to couple the spins to form a singlet state ($S = 0$). We have chosen the spin coupling $^1(xa)^1(yb)$, which signifies coupling the spins of orbitals x and a to form $S = 0$ and then coupling the spins of orbitals y and b to form $S = 0$. For the excitation from x^2y^2 to $xyab$, there are two easily interpreted, but nonorthogonal, results, $^1(xa)^1(yb)$ and $^1(xb)^1(ya)$. One of these discussed above is the double charge transfer with the larger coefficient. The second is double excitation of 5σ to $2\pi^*$ and $3dt_{2g}$ to $3d^*e_g$. This is a dispersion-type configuration representing angular correlation between the $5\sigma e_g$ and $3dt_{2g}$ electrons and has a coefficient that will vanish like an inverse power of R.

IV. Conclusions

The previous calculation of the binding energy of $Cr(CO)_6$ reported in part 1 was improved using a better bond length for the CO and including correlation correction.

The total binding energy was calculated to be 117 and 146 kcal/mol using the MRSD-CI and QDVARPT methods, respectively. These results represent around 72% and 90% of the experimental value. These results are comparable with the best

result reported recently by Barnes et al.[5] at the CCSD(T) level which represent 77% of the experimental value after BSSE correction.

From these results, we can conclude that the predominant source of the correlation correction to the bonding came from the correlation between electrons in the orbitals $5\sigma e_g$ and $3dt_{2g}$ using the virtual K orbitals $2\pi^*t_{2g}$ and $3d^*e_g$.

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