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Combining Multiconfigurational Wave Functions with Density Functional Estimates of Dynamic Electron Correlation. 2. Effect of Improved Valence Correlation

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We present further tests of a recently introduced scheme (*J. Phys. Chem.* **1996**, *100*, 10131) for combining multiconfigurational wave functions with density functional estimates of the dynamic electron correlation. We investigate the equilibrium geometries and bond dissociation energies for selected bonds in a series of 25 molecules at the CASSCF level and also with the new method (which we term CASΔDF). The CASΔDF method approximately halves the error in R_e and D_e with respect to the CASSCF level. We have also investigated the role of improving the valence correlation through extension of the active space used in the CASSCF reference wave function. Again the CASΔDF method produces a halving of the mean errors in R_e and D_e with respect to the CASSCF level.

Introduction

Many systems are poorly described by the single-determinant Hartree−Fock (HF) theory. For such systems the multiconfigurational self-consistent field (MCSCF) method usually gives a reliable reference wave function. The added expense of the MCSCF treatment means that the size of system that may be studied is considerably smaller but, with a well-chosen partitioning of the orbitals and electrons, modern computer programs can efficiently model a large variety of chemical processes. MCSCF theory and its complete active space variant (CASSCF) are effective techniques for dealing with the nondynamic correlation but are not suitable for treating the dynamic electron correlation problem.[1] The multireference forms of configuration interaction (CI),[2] perturbation theory (PT),[3−5] and coupled cluster theory (CC)[6,7] are orders of magnitude more expensive than their single-reference counterparts and are therefore restricted to much smaller systems than the MCSCF method.

Currently there is a great deal of interest in the use of density functionals for the inclusion of correlation effects. Generally these calculations are performed in a self-consistent manner within the Kohn−Sham formalism. It is also possible to obtain the correlation energy using the HF density and a correlation functional, giving the total energy as

$$E_{\text{Total}} = E_{\text{HF}} + E_{\text{C}}(\rho_{\text{HF}}) \tag{1}$$

where the correlation energy, $E_{\text{C}}(\rho_{\text{HF}})$, is a functional of the one-electron density

$$E_{\text{C}}(\rho) = \int \rho \epsilon_{\text{C}}(\rho)\, \mathrm{d}V \tag{2}$$

and $\epsilon_{\text{C}}(\rho)$ is the correlation energy per electron. $\epsilon_{\text{C}}(\rho)$ is usually a complicated function of ρ and sometimes $\nabla\rho$.[8] However, the use of the MCSCF one-electron density in eq 1 will overestimate the correlation energy, since the MCSCF wave function already contains a component of the electron correlation.

In the next section we outline our recently introduced[9] scheme for the introduction of dynamic correlation effects, which we term CASΔDF. We then apply this method to the equilibrium geometries and bond dissociation energies for selected bonds in a series of 25 molecules. One of the main considerations when performing MCSCF (or CASSCF) calculations is the choice of active space. We investigate the effect of using improved active spaces on our set of 25 molecules.

Computational Details

In this section we briefly outline the CASΔDF scheme. The reader is referred to ref 9 for a fuller exposition. We begin by writing the total density of the system as

$$\rho = \rho_{\text{core}} + \rho_{\text{valence}} \tag{3}$$

where the "core" and "valence" separation is dictated by the orbital partitioning of the CASSCF calculation. The total energy is obtained as

$$E_{\text{CAS}\Delta\text{DF}} = E_{\text{CASSCF}} + E_{\text{C}}(\rho) - E_{\text{C}}(\rho_{\text{valence}}) \tag{4}$$

The density functional we have used in the present study is the Wilson−Levy correlation functional[10]

$$E_{\text{C}}(\rho) = \int \frac{(a\rho + b|\nabla\rho|\rho^{-1/3})}{(c + d|\nabla\rho|(\rho/2)^{-4/3} + r_{\text{s}})} \tag{5}$$

where $r_{\text{s}} = (3/4\pi\rho)^{1/3}$, $a = -0.748\,60$, $b = 0.060\,01$, $c = 3.600\,73$, and $d = 0.900\,000$. Fuentealba and Savin[11] have shown that this is an excellent functional for use with HF densities. All calculations have been performed using the CASSCF option in our valence bond codes,[12,13] which we have interfaced with the GAUSSIAN 94 suite of programs.[14] For the numerical integration of eq 5, we have used the partitioning of the integrand described by Becke[15] with a 128-point Euler−MacLaurin quadrature[16] for the radial component and a 302-point Lebedev quadrature[17] for the angular components. The minimum energy geometries were located using numerical gradients and the Fletcher−Powell minimization algorithm[18] as implemented in GAUSSIAN 94. All calculations reported in this paper have employed the 6-31G** basis set.[19] This is a commonly used basis of medium size and so illustrates the general utility of the approach.

Results

We have previously[9] applied the CASΔDF scheme to calculating the equilibrium bond length and bond dissociation

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TABLE 1: Total Energies (au), Selected Bonds, Corresponding Bond Lengths (Å), and Bond Dissociation Energies (kcal mol^{-1}) Obtained at the CASSCF/6-31G Level with Minimal Active Spaces (See Text)**[a]

molecule	bond	energy	R_e	R_e (exptl)	$\lvert\Delta R_e\rvert$	D_e	D_e (exptl)	ΔD_e
LiH (2, 2)	Li−H	−7.997 844	1.66	1.60	0.07	42.8	57.6	14.8
BeH (2, 2)	Be−H	−15.147 427	1.34	1.34	0.00	51.6	50.0	−1.6
BH_3 (6, 6)	B−H	−26.437 424	1.21			100.0	112.8	12.8
NH_3 (6, 6)	N−H	−56.267 019	1.02	1.01	0.01	101.8	116.3	14.5
H_2O (4, 4)	O−H	−76.073 654	0.97	0.96	0.01	105.5	125.7	20.2
HF (2, 2)	F−H	−100.034 681	0.92	0.92	0.00	109.6	140.9	31.3
HCl (2, 2)	Cl−H	−460.082 371	1.29	1.28	0.01	87.8	106.4	18.6
Li_2 (2, 2)	Li−Li	−14.877 917	2.97	2.67	0.30	9.5	24.4	14.9
C_2H_6 (2, 2)	C−C	−79.253 575	1.55	1.53	0.03	83.5	96.5	13.0
C_2H_4 (4, 4)	C−C	−78.093 270	1.35	1.33	0.02	158.3	179.8	21.5
C_2H_2 (6, 6)	C−C	−76.924 507	1.22	1.20	0.02	233.0	234.4	1.4
N_2H_4 (2, 2)	N−N	−111.205 957	1.45	1.45	0.01	52.6	75.1	22.5
N_2H_2 (4, 4)	N−N	−110.079 431	1.26	1.25	0.01	105.3	118.0	12.7
N_2 (6, 6)	N−N	−109.079 407	1.12	1.09	0.02	197.5	228.4	30.9
H_2O_2 (2, 2)	O−O	−150.819 690	1.50	1.45	0.05	31.7	55.1	23.4
F_2 (2, 2)	F−F	−198.750 742	1.49	1.42	0.08	17.1	38.2	21.2
Cl_2 (2, 2)	Cl−Cl	−918.936 025	2.07	1.99	0.08	29.9	58.0	28.1
CH_3NH_2 (2, 2)	C−N	−95.239 836	1.48	1.47	0.01	74.6	93.2	18.6
CH_2NH (4, 4)	C−N	−94.099 370	1.29	1.27	0.02	140.1	153.3	13.2
HCN (6, 6)	C−N	−92.998 056	1.17	1.15	0.02	212.8	227.3	14.5
CH_3OH (2, 2)	C−O	−115.067 835	1.43	1.42	0.01	77.2	98.0	20.8
CH_2O (4, 4)	C−O	−113.942 341	1.22	1.20	0.02	152.4	183.7	31.3
CO (6, 6)	C−O	−112.858 875	1.14	1.13	0.01	252.8	259.2	6.5
CH_3F (2, 2)	C−F	−139.064 083	1.40	1.38	0.01	89.1	113.9	24.8
ClF (2, 2)	Cl−F	−558.856 579	1.69	1.63	0.07	31.7	60.2	28.5
				mean	0.04		mean	18.5
				max	0.30		max	31.3

[a] Values in parentheses in column 1 refer to the number of active electrons and orbitals.

energy of eight diatomic molecules, using reasonably large basis sets. Comparing with the CASSCF results, the mean absolute error in R_e was improved from 0.023 to 0.019 Å, and the mean absolute error in D_e was improved from 24.9 to 7.3 kcal mol^{-1}. As a further test of the CASΔDF scheme, we present an investigation of the structure and energetics of 25 small molecules. We have studied the dissociation of a selected bond in each molecule. The molecules studied contain single and multiple, hetero- and homonuclear bonds. We have chosen the series of molecules such that they include a large variety of bonds with systematic differences in the bonding type, covering most of the characteristics to be found in larger organic and inorganic species. We note that the calculation of the dissociation energy of a selected bond is a more demanding problem than calculating the atomization energy (which is often used for assessing the accuracy of new methods). When only a selected bond is broken, it is necessary to correctly describe the molecule in its fragment states as well as in its equilibrium geometry. The electronic structure of these fragment states is a more difficult problem than that of the isolated atoms

Minimal Active Spaces. We have initially chosen minimal active spaces consisting of the bonding and antibonding orbitals for each electron pair in the selected bond. The only exceptions to this are for those molecules where the selected bond is nonunique, e.g. the N−H bond in ammonia, where the active space includes electrons and orbitals corresponding to all identical bonds.

For each molecule, details of the selected bond, active space used, total energy, equilibrium bond length, bond dissociation energy, and associated errors with respect to experiment are given in Tables 1 and 2 for the CASSCF and CASΔDF methods, respectively. The *mean* absolute error in bond lengths is reduced from 0.04 Å, at the CASSCF level, to 0.02 Å, at the CASΔDF level. The bond lengths at the CASSCF level tend to be too long, and inclusion of dynamic correlation shortens them, in line with expectation. The *maximum* absolute error in the bond lengths is reduced from 0.30 Å at the CASSCF level to 0.18 Å using CASΔDF. This large maximum error arises from the poor estimate of the equilibrium geometry for Li_2. While this error is almost halved through the inclusion of dynamic correlation, this is not sufficient to overcome the inadequacy of the simple two-electron two-orbital reference wave function used. The proper form of the reference wave function has been discussed by Lie and Clementi[20] and will be considered in the next section.

The *mean* absolute error in the bond dissociation energies is improved from 18.5 kcal mol^{-1} at the CASSCF level to 7.9 kcal mol^{-1} using CASΔDF. As is to be expected, the CASSCF results underestimate the bond dissociation energies. The inclusion of dynamic correlation at the CASΔDF level always deepens the potential energy well and only overestimates the experimental dissociation energies for 4 of the 25 molecules. The *maximum* absolute error in the bond dissociation energies is reduced from 31.3 kcal mol^{-1} at the CASSCF level to 18.9 kcal mol^{-1} using CASΔDF. The reduction in the errors shows a similar trend to those found for the eight diatomics in ref 9.

Improved Valence Correlation. The use of the CASΔDF method clearly has a dramatic effect on the geometries and bond dissociation energies for the molecules studied. Further improvements could be introduced by refining the density functional used or by improving the wave function from which the valence electron correlation energy is obtained. In this section we address the latter problem only. In the CASSCF formalism the simplest way to improve the correlation of the valence electrons is through the expansion of the active space.

To examine the effects of using different active spaces, we have included virtual σ and π orbitals for Li_2 and LiH (which are necessary for a proper reference function).[20,21] For most other atoms, the active space has been enlarged by including lone-pair electrons that were treated as "core" (inactive) in the previous calculations. For each lone pair added we have included a corresponding correlating orbital from the virtual manifold. The inclusion of lone-pair electrons (and the associated pair of orbitals) increases considerably the size of the CASSCF configuration expansion; e.g., for F_2 the addition of

TABLE 2: Total Energies (au), Selected Bonds, Corresponding Bond Lengths (Å), and Bond Dissociation Energies (kcal mol^{-1}) Obtained at the CASΔDF/6-31G Level with Minimal Active Spaces (See Text)[a]**

molecule	bond	energy	R_e	R_e (exptl)	$\lvert\Delta R_e\rvert$	D_e	D_e (exptl)	ΔD_e
LiH (2, 2)	Li−H	−8.045 437	1.64	1.60	0.05	46.3	57.6	11.3
BeH (2, 2)	Be−H	−15.195 930	1.33	1.34	0.01	55.8	50.0	−5.8
BH_3 (6, 6)	B−H	−26.485 774	1.20			111.7	112.8	1.1
NH_3 (6, 6)	N−H	−56.410 658	1.02	1.01	0.01	105.2	116.3	11.1
H_2O (4, 4)	O−H	−76.325 904	0.96	0.96	0.00	112.4	125.7	13.3
HF (2, 2)	F−H	−100.370 525	0.91	0.92	0.00	122.0	140.9	18.9
HCl (2, 2)	Cl−H	−460.810 637	1.26	1.28	0.01	101.9	106.4	4.5
Li_2 (2, 2)	Li−Li	−14.968 697	2.85	2.67	0.18	13.7	24.4	10.7
C_2H_6 (2, 2)	C−C	−79.889 911	1.52	1.53	0.01	95.6	96.5	0.9
C_2H_4 (4, 4)	C−C	−78.569 636	1.33	1.33	0.00	170.6	179.8	9.2
C_2H_2 (6, 6)	C−C	−77.203 802	1.21	1.20	0.01	240.6	234.4	−6.2
N_2H_4 (2, 2)	N−N	−111.863 755	1.41	1.45	0.04	71.6	75.1	3.5
N_2H_2 (4, 4)	N−N	−110.572 421	1.25	1.25	0.01	124.3	118.0	−6.3
N_2 (6, 6)	N−N	−109.364 480	1.10	1.09	0.01	215.4	228.4	13.0
H_2O_2 (2, 2)	O−O	−151.474 791	1.43	1.45	0.02	48.5	55.1	6.6
F_2 (2, 2)	F−F	−199.400 652	1.42	1.42	0.00	28.1	38.2	10.1
Cl_2 (2, 2)	Cl−Cl	−920.381 428	1.95	1.99	0.04	51.2	58.0	6.8
CH_3NH_2 (2, 2)	C−N	−95.886 184	1.45	1.47	0.02	89.7	93.2	3.6
CH_2NH (4, 4)	C−N	−94.583 178	1.27	1.27	0.00	155.2	153.3	−1.9
HCN (6, 6)	C−N	−93.279 950	1.16	1.15	0.01	225.4	227.3	1.9
CH_3OH (2, 2)	C−O	−115.712 668	1.41	1.42	0.02	91.1	98.0	6.9
CH_2O (4, 4)	C−O	−114.424 553	1.21	1.20	0.01	166.8	183.7	16.9
CO (6, 6)	C−O	−113.136 373	1.13	1.13	0.01	255.0	259.2	4.2
CH_3F (2, 2)	C−F	−139.708 618	1.35	1.38	0.03	101.7	113.9	12.2
ClF (2, 2)	Cl−F	−559.905 768	1.63	1.63	0.00	48.9	60.2	11.3
				mean	0.02		mean	7.9
				max	0.18		max	18.9

[a] Values in parentheses in column 1 refer to the number of active electrons and orbitals.

TABLE 3: Total Energies (au), Selected Bonds, Corresponding Bond Lengths (Å), and Bond Dissociation Energies (kcal mol^{-1}) Obtained at the CASSCF/6-31G Level with Extended Active Spaces (See Text)[a]**

molecule	bond	energy	R_e	R_e (exptl)	$\lvert\Delta R_e\rvert$	D_e	D_e (exptl)	ΔD_e
LiH (2, 4)	Li−H	−8.003 974	1.62	1.60	0.03	46.7	57.6	10.9
BeH (2, 2)	Be−H	−15.147 427	1.34	1.34	0.00	51.6	50.0	−1.6
BH_3 (6, 6)	B−H	−26.437 424	1.21			100.0	112.8	12.8
NH_3 (8, 8)	N−H	−56.300 140	1.02	1.01	0.01	107.3	116.3	9.0
H_2O (6, 6)	O−H	−76.098 745	0.96	0.96	0.00	111.6	125.7	14.1
HF (6, 6)	F−H	−100.101 023	0.92	0.92	0.00	127.9	140.9	13.0
HCl (6, 6)	Cl−H	−460.111 342	1.27	1.28	0.01	98.2	106.4	8.2
Li_2 (2, 5)	Li−Li	−14.892 259	2.73	2.67	0.06	21.0	24.4	3.4
C_2H_6 (2, 2)	C−C	−79.253 575	1.55	1.53	0.03	83.5	96.5	13.0
C_2H_4 (4, 4)	C−C	−78.093 270	1.35	1.33	0.02	158.3	179.8	21.5
C_2H_2 (6, 6)	C−C	−76.924 507	1.22	1.20	0.02	233.0	234.4	1.4
N_2H_4 (6, 6)	N−N	−111.242 840	1.46	1.45	0.01	62.5	75.1	12.6
N_2H_2 (8, 8)	N−N	−110.122 284	1.26	1.25	0.01	103.3	118.0	14.7
N_2 (10, 10)	N−N	−109.116 931	1.12	1.09	0.02	212.1	228.4	16.3
H_2O_2 (2, 2)	O−O	−150.819 690	1.50	1.45	0.05	31.7	55.1	23.4
F_2 (10, 10)	F−F	−198.854 440	1.43	1.42	0.02	35.4	38.2	2.8
Cl_2 (10, 10)	Cl−Cl	−918.975 994	2.06	1.99	0.07	39.4	58.0	18.6
CH_3NH_2 (4, 4)	C−N	−95.260 005	1.48	1.47	0.01	80.4	93.2	12.8
CH_2NH (6, 6)	C−N	−94.122 927	1.29	1.27	0.02	140.3	153.3	13.0
HCN (6, 6)	C−N	−92.998 056	1.17	1.15	0.02	212.8	227.3	14.5
CH_3OH (4, 4)	C−O	−115.097 314	1.44	1.42	0.02	81.4	98.0	16.6
CH_2O (8, 8)	C−O	−114.009 307	1.22	1.20	0.01	175.5	183.7	8.2
CO (6, 6)	C−O	−112.858 875	1.14	1.13	0.01	252.8	259.2	6.5
CH_3F (6, 6)	C−F	−139.132 524	1.39	1.38	0.01	108.7	113.9	5.2
ClF (10, 10)	Cl−F	−558.939 651	1.66	1.63	0.03	52.7	60.2	7.5
				mean	0.02		mean	11.3
				max	0.07		max	23.4

[a] Values in parentheses in column 1 refer to the number of active electrons and orbitals.

the two lone pairs on each atom results in an expansion containing 19 404 configurations compared with only 3 when the lone pairs are kept within the core (inactive) space. The results using the expanded valence spaces are given in Tables 3 and 4 for CASSCF and CASΔDF, respectively. The number of electrons and orbitals included in the active spaces are also given. The *mean* absolute error in the bond lengths is now improved from 0.02 Å at the CASSCF level to 0.01 Å using CASΔDF. These errors are approximately half those found using the minimal active spaces. The *maximum* error is now reduced from 0.07 Å at the CASSCF level to 0.04 Å using CASΔDF. The improvement of the valence correlation through the expansion of the active space clearly has a significant effect on the predicted R_e at both levels of theory showing that, given a good reference function, the CASΔDF approach is quite reliable.

The *mean* absolute error in the bond dissociation energies is reduced from 11.3 kcal mol^{-1} at the CASSCF level to 5.4 kcal

TABLE 4: Total Energies (au), Selected Bonds, Corresponding Bond Lengths (Å), and Bond Dissociation Energies (kcal mol^{-1}) Obtained at the CASΔDF/6-31G Level with Extended Active Spaces (See Text)[a]**

molecule	bond	energy	R_e	R_e (exptl)	$\|\Delta R_e\|$	D_e	D_e (exptl)	ΔD_e
LiH (2, 4)	Li−H	−8.051 660	1.61	1.60	0.01	50.2	57.6	7.4
BeH (2, 2)	Be−H	−15.195 930	1.33	1.34	0.01	55.8	50.0	−5.8
BH_3 (6, 6)	B−H	−26.485 774	1.20			111.7	112.8	1.1
NH_3 (8, 8)	N−H	−56.317 533	1.03	1.01	0.01	105.1	116.3	11.2
H_2O (6, 6)	O−H	−76.251 401	0.96	0.96	0.00	116.0	125.7	9.7
HF (6, 6)	F−H	−100.241 060	0.92	0.92	0.01	125.1	140.9	15.8
HCl (6, 6)	Cl−H	−460.659 731	1.26	1.28	0.02	103.2	106.4	3.2
Li_2 (2, 5)	Li−Li	−14.984 459	2.67	2.67	0.01	26.1	24.4	−1.7
C_2H_6 (2, 2)	C−C	−79.889 911	1.52	1.53	0.01	95.6	96.5	0.9
C_2H_4 (4, 4)	C−C	−78.569 636	1.33	1.33	0.00	170.6	179.8	9.2
C_2H_2 (6, 6)	C−C	−77.203 802	1.21	1.20	0.01	240.6	234.4	−6.2
N_2H_4 (6, 6)	N−N	−111.757 705	1.43	1.45	0.02	77.0	75.1	−1.9
N_2H_2 (8, 8)	N−N	−110.424 511	1.26	1.25	0.01	125.9	118.0	−7.9
N_2 (10, 10)	N−N	−109.170 802	1.11	1.09	0.01	223.6	228.4	4.8
H_2O_2 (2, 2)	O−O	−151.474 791	1.43	1.45	0.02	48.5	55.1	6.6
F_2 (10, 10)	F−F	−199.152 200	1.43	1.42	0.01	40.9	38.2	−2.7
Cl_2 (10, 10)	Cl−Cl	−920.072 129	1.95	1.99	0.04	49.0	58.0	9.0
CH_3NH_2 (4, 4)	C−N	−95.835 560	1.45	1.47	0.02	93.7	93.2	−0.5
CH_2NH (6, 6)	C−N	−94.508 067	1.28	1.27	0.01	155.1	153.3	−1.8
HCN (6, 6)	C−N	−93.279 950	1.16	1.15	0.01	225.4	227.3	1.9
CH_3OH (4, 4)	C−O	−115.664 725	1.41	1.42	0.01	92.5	98.0	5.5
CH_2O (8, 8)	C−O	−114.259 569	1.22	1.20	0.01	175.3	183.7	8.4
CO (6, 6)	C−O	−113.136 373	1.13	1.13	0.01	255.0	259.2	4.2
CH_3F (6, 6)	C−F	−139.586 199	1.38	1.38	0.01	109.1	113.9	4.8
ClF (10, 10)	Cl−F	−559.631 291	1.64	1.63	0.01	57.0	60.2	3.2
				mean	0.01		mean	5.4
				max	0.04		max	15.8

[a] Values in parentheses in column 1 refer to the number of active electrons and orbitals.

mol^{-1} using CASΔDF. As with the smaller active spaces, the CASSCF results generally underestimate the bond dissociation energies. The inclusion of dynamic correlation deepens the potential energy well and gives considerable improvement in the predicted dissociation energies. The *maximum* absolute error in the bond dissociation energies is reduced from 23.4 kcal mol^{-1} at the CASSCF level to 15.8 kcal mol^{-1} using CASΔDF.

Conclusion

The results presented in the previous sections are very encouraging, considering the limitation of the basis set employed. For example, earlier calculations[9] on D_e of the HF molecule (which has the largest errors at both the CASSCF and CASΔDF levels) shows a ≈3 kcal mol^{-1} improvement over the 6-31G** results when a cc-pVTZ basis[22,23] is used.

The question of improvement of the correlation functional used in the CASΔDF method is still open; however, we have found the Wilson−Levy functional to be the most successful for our purposes. We intend to investigate other denisty functionals in the next paper in this series. We are also investigating the use of the CASΔDF method for studying reaction barriers and systems highly sensitive to both dynamic and nondynamic correlation effects. Finally we note that the form of the ΔDF equation means that it could, in principle, be applied to any reference wave function for which it is possible to partition the electrons into "core" and "valence" sets. This can mean any multiconfigurational wave function of the MCSCF type.

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