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Accurate numerical orbital MBPT/CC study of the electron affinity of fluorine and the dissociation energy of hydrogen fluoride^{a)}

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The classic problem of the dissociation energy of FH and the electron affinity of F have been studied using our recent proposed numerical orbital coupled-cluster (CC) method. With 105 orbitals, 96.6% of the correlation energy of FH is obtained, and exact agreement with the experimental dissociation energy. Similarly, the electron affinity of F is found to be 3.37 eV compared to an experimental value of 3.399 eV.

I. INTRODUCTION

The dissociation energy of FH and the electron affinity of fluorine are two of the classic problems in *ab initio* quantum chemistry. As Benson¹ suggests, "*Ab initio* methods for solving the Schrödinger equation are not yet capable of providing values of ΔH_f to better than ± 4 kcal/mol even for relatively simple species."

Similarly, even though relatively small basis correlated calculations often give an electron affinity of F that is close to the experimental value of 3.4 eV,² once the basis set is extended, the agreement with experiment typically degenerates to a value of 3.1 to 3.2 eV,³⁻⁵ indicating that the basis set limit for F⁻ is extremely hard to achieve, or that some important correlation corrections⁵ are missing, such as might be incorporated in a size-extensive coupled-cluster (CC) or many-body perturbation theory (MBPT) method. In this paper, we employ our recently proposed numerical orbital MBPT/CC techniques^{6,7} to attempt to approach the basis set limit for these two classic problems.

Calculations in molecular quantum chemistry are dominated by the basis set approach. The most often used are Gaussian orbitals, which offer very fast procedures for the evaluation of one- and two-electron integrals. The basis set approach significantly simplifies the approximate solution of the Schrödinger equation as it allows the multielectron problem to be transformed into a system of matrix equations. However, the initial choice of basis functions determines the ultimate accuracy of a calculated property, and basis set errors are difficult to control. The proper choice of well-balanced basis set poses a particularly difficult problem when a property is related to a drastic change in electronic structure. The formation of a molecule out of atoms, or the formation of an anion by electron attachment exemplify such processes where a single basis set is asked to describe very different situations. An alternative would be to adjust the basis functions to accommodate the wave function change during the chemical reaction. However, if such an adjustment is allowed, it should preserve the precision balance, i.e., the calculations along the reaction path should be done at the same level of accuracy, which is clearly necessary for electron affinities and dissociation energies.

Recently, we proposed a numerical method⁶⁻⁸ which

uses adjustable numerical orbitals in MBPT and CC calculations.⁹⁻¹¹ The method is based on the concept of the Bethe-Goldstone (BG) hierarchy of cluster equations¹² and on the MCSCF method with numerical orbitals.¹³ The union of these and the MBPT and CC methods allows one to calculate electronic correlation energies of simple diatomics with exceptional accuracy.⁶⁻⁸ For example, the value of -0.082 16 a.u. for the correlation energy for the LiH molecule has been obtained at the CCSDT-1 level¹⁴ (CC method with single, double, and triple excitation operators, the latter with some restrictions) which agrees with the experimental value of 0.0832 a.u. to within 1%.

In the present paper we demonstrate the application of this method to the fluorine electron affinity and the dissociation energy of FH. Both problems have been subject to many theoretical studies in the past (see, for example, Refs. 3-5 and 15-17, and references therein). Dunning's atomization energy for the FH molecule¹⁵ evaluated with the SDCl method built upon a GVB wave function is more than 10 kcal/mol from the experimental results due to the basis set deficiency and the size extension error. The theoretical estimation of Pople *et al.*¹⁷ for the FH dissociation energy agrees perfectly with experiment, but has been obtained by assuming the additivity of the energy contributions arising from different basis set extensions, which introduces an approximation. Also, basis set superposition for such dissociation energies typically result in an effect of 1-2 kcal/mol,¹⁶ usually artificially improving agreement with experiment.

Systematic studies of the fluorine electron affinity have been reported by Sasaki and Yoshimine,⁵ Roos *et al.*,⁴ and Kucharski *et al.*³ With the best results clustering near 3.1 to 3.2 eV, or 0.2 eV from experiment. Therefore, one may conclude that an extensive correlated treatment together with a reliable basis set is required to get adequate agreement with the experimental data. The present calculations offer such possibilities.

II. COMPUTATIONAL DETAILS

The following partial wave expansion form of numerical orbitals for a diatomic system is utilized in the present calculations:

$$\psi^m(\xi, \eta, \phi) = \sum_{L=|m|}^{L_n} X_L^m(\xi) Y_L^m(\eta, \phi), \quad (1)$$

where (ξ, η, ϕ) are prolate, spheroidal coordinates, Y_L^m are the usual normalized spherical harmonics, and X_L^m are un-

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known numerical functions to be determined. The subscript m denotes the orbital symmetry ($m = 0$ for σ orbitals, ± 1 for π orbitals, etc.). The numerical orbital generation procedure in conjunction with the MBPT/CC methods has been described previously.⁶⁻⁸ Here we briefly summarize the procedure and some specifics are given in relation to the systems under investigation.

Step 1: Numerical RHF calculation

For both the fluorine atom and the anion, the diatomic numerical Hartree-Fock (HF) program has been used, with two-center partial wave expansions for orbitals. Therefore, the atomic spherical symmetry was not explicitly forced and the variation of the orbital $2p_0$ is formally independent from the variation of the $2p_{\pm 1}$ shell. Such an approach provides a consistent treatment of the FH molecule, F, and F^- . The HF single-determinantal reference functions optimized for F, F^- , and FH have the following orbital occupancies:

$$F: 1s^2 2s^2 2p_0 2p_{\pm 1};$$

$$F^-: 1s^2 2s^2 2p_0^2 2p_{\pm 1};$$

$$FH: 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4.$$

Step 2: Bethe-Goldstone partition of the total electron correlation into clusters

The following cluster structure has been applied:

$$F: (1s^2), (2s^2), (2p_{\pm 1}), (1s2s), (1s2p_0), (2s2p_0),$$

$$(2s2p_{\pm 1}), (2p_0 2p_{\pm 1});$$

$$F^-: \text{same as for the fluorine atom plus } (2p_0^2);$$

$$FH: (1\sigma^2) (2\sigma^2) (3\sigma^2) (1\pi^4) (1\sigma 2\sigma) (1\sigma 3\sigma) (1\sigma 1\pi) \\ (2\sigma 3\sigma) (2\sigma 1\pi) (3\sigma 1\pi).$$

This partition was designed to reflect the physical nature of electron correlation. One may notice that all clusters but one involve two electrons.

Step 3: Independent variational calculations using the numerical MCSCF method are performed for each cluster

The orbitals of the reference determinant are kept frozen and excitations only within the correlated cluster are considered. The series of MCSCF calculations results in sets of correlating numerical orbitals. Orbitals, which belong to different sets, are not orthogonal, but all correlation orbitals are orthogonal to the orbitals of the reference determinant.

Step 4: MBPT and CC calculations in the combined orbital space

The orbitals of the HF reference determinant and correlating MCSCF orbitals are combined and numerically orthogonalized. In the case of the fluorine atom, where the correlation of the $(2p_0^2)$ cluster is not present, the orbitals which correlate the $(3\sigma^2)$ cluster for the FH molecule are added. This equalizes the total number of orbitals for each system, making it equal to 105 functions (19σ , 21π , 17σ , and 5ϕ). Once the final orbital set is constructed, the one- and two-electron integrals are calculated and the SCF calculation is performed (RHF for F^- and FH and UHF for F). The resulting canonical SCF orbitals are then used in the MBPT and CC calculations.

TABLE I. MBPT and CC total and correlation energies for the fluorine atom, fluorine anion, and hydrogen fluoride in a.u. Numbers in parentheses are correlation corrections for the MBPT method and total correlation energies for the CC method.

	F	F^-	FH ($R = 1.7328$ a.u.)
SCF	-99.416 257	-99.459 561	-100.070 807
MBPT:			
D(2)	-99.696 921 (-0.289 664)	-99.832 616 (-0.373 155)	-100.429 767 (-0.358 960)
D(3)	-99.706 901 (-0.009 980)	-99.820 432 (+0.012 184)	-100.428 663 (+0.001 103)
SDTQ(4)	-99.707 451 (-0.005 537)	-99.841 684 (-0.021 252)	-100.440 234 (-0.011 570)
MBPT(4) correlation energy	(-0.305 181)	(-0.382 223)	(-0.369 427)
CC:			
CCSD	-99.707 610 (-0.291 352)	-99.824 666 (-0.365 205)	-100.430 236 (-0.359 429)
CCSD + T(CCSD)	-99.712 831 (-0.296 574)	-99.836 789 (-0.377 328)	-100.438 777 (-0.367 970)
Exact correlation energy	-0.310 ^a	-0.398 \pm 0.003 ^b	-0.381 ^c
(Calculated corr. energy)/(Exact corr. energy) %			
MBPT(4)	98.4%	96.0% \pm 0.8%	97.0%
CCSD + T(CCSD)	95.7%	94.8% \pm 0.8%	96.6%

^a Clementi's correlation energy (Ref. 22) corrected for a UHF reference state used in the present calculations would be -0.317. We obtain -0.310 from the correlation value 0.381 for FH and the experimental dissociation energy for FH.

^b From Ref. 21.

^c From Ref. 23.

III. NUMERICAL RESULTS

As we demonstrated before for the LiH molecule, the BG correlating orbitals appear to constitute a very accurate basis set for the CC calculation. However, the low-order MBPT results are relatively less accurate. This tendency works in the opposite direction if the basis set is optimized for the second-order MBPT correlation function. For example, calculations performed by Jeziorski *et al.*¹⁸ indicate that the optimization of the basis set for the first-order functional correlation correction, which results in a virtually exact value of $E^{(2)}$, gives a less accurate correlation energy at the CC level.

In Table I we present MBPT results through fourth-order and CC results obtained at the CCSD level (single and double excitations) and at the CCSD + T(CCSD) level,¹⁹ where the contribution of triple excitations is included in the last CCSD iteration. This model is found to be numerically essentially the same¹⁹ as our CCSDT-1 (model that includes iterative effects of T_3 ¹⁴). Upon inspection of the MBPT correlation corrections, it is apparent that the character of the convergence of the perturbation expansion is different for F, F⁻, and FH. Therefore it is not surprising that the reproduction of the correlation energy by the CCSD + T(CCSD) model is also different. We get as much as 96.6% of the experimental correlation energy for the FH molecule. The percentage is slightly lower for the other systems. Furthermore, our second-order MBPT energy, equal to 0.358 96 a.u., is significantly better than the best calculated result 0.331 a.u. of McCullough *et al.*,²⁰ who used natural orbital expansions for correlated pair functions and solved the first-order pair equations numerically, except in a smaller one-electron space.

We present in Table II results for the electron affinity of the fluorine atom and for the dissociation energy of hydrogen fluoride. The final CCSD + T(CCSD) result for the fluorine electron affinity differs from experiment by 0.8%. The experimental result for the fluorine electron affinity has not been corrected for spin-orbit interaction, in agreement with the suggestion²¹ that this correction should be negligible for the first row atoms. If corrected, the experimental value would be 3.41 eV. The basis set results of Raghavachari²⁷ using similar MBPT/CC methods give 3.35–3.45 eV.

The dissociation energy (D_e) for FH is in embarrassingly perfect agreement with experiment.²⁴ Of course, since we have an error of 3.4% in the FH correlation energy, perfect agreement simply means we have essentially the same error in the F atom energy, permitting the errors to cancel. In fact, the correlation energy in each case is in error by about 8 kcal/mol but the consistent treatment of F and FH facilitated by numerical orbitals permits much error cancellation.

It is interesting that MBPT(4) overshoots D_e by 4.3 kcal/mol. Elsewhere, we have shown that MBPT(4) overestimates the DZP full CI correlation energy for FH, which is only corrected by MBPT(5) or CC theory.²⁵ Such an overestimate here coupled with a likely underestimate of the open-shell F atom energy probably accounts for this result. We have found this overestimate to be largely due to the fact that the normally neglected fifth- and higher-order triple excitation contributions typically reduce the magnitude of the

TABLE II. Electron affinity of the fluorine atom and dissociation energy of hydrogen fluoride calculated at different levels of MBPT and CC methods.

	F + e ⁻ → F ⁻ (eV)	F + H → FH (kcal/mol)
SCF	1.176	97.0
MBPT:		
D(2)	3.692	146.2
D(3)	3.089	139.2
SDTQ(4)	3.653	146.1
CC:		
CCSD	3.185	139.7
CCSD + T(CCSD)	3.373	141.8
Experiment	3.399 ^a	141.8 ^b

^a See Ref. 2. Hotop and Lineberger recommend a corrected electron affinity of 3.410 once the spin-orbit interaction is excluded to compare with spin-independent *ab initio* calculations. However, Clementi and McLean (Ref. 21) suggests that the spin-orbit correction should be negligible for the first-row elements. These authors recommend 3.37 for the electron affinity.

^b See Ref. 24.

fourth-order triples contribution to the correlation energy. CCSDT-1 and CCSD + T(CCSD) incorporate this effort. Also, since the numerical orbital basis should approach completeness, the present results should be largely free from superposition errors.²⁶

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