Vol.16 No.3 NUCLEAR SCIENCE AND TECHNIQUES June 2005

Studies of structure, vibrational frequencies and thermodynamics of UF_6

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Abstract After molecular structure of UF_6 is optimized, molecular vibrational frequencies are calculated by LDA and GGA approaches. Some thermodynamic parameters are calculated based on the principle of statistic mechanics. Various functionals such as PWC, VWN, VWNPB, PW91, BP, PBE, RPBE, BOP with various basis sets such as MIN, DN, DND and DNP are used. The small basis sets, MIN and DN, can arrive at self-consistency. DMol^3 can save more CPU's time and resource than all electron calculations including Hartree-Fock and DFT with Gaussian code, so it should be introduced in some research, especially on compounds of lanthanide and actinide. However, comparing with the results from classical DFT, the new calculation may accompany a rather large error.

Key words Structure, Vibrational frequency, Thermodynamic parameters, Uranium hexafluoride

CLC number O614.62

1 Introduction

The success that density functional theory (DFT) has been applied to calculations of accurate structures, thermodynamic parameters and vibrational properties of molecules has impelled investigators to use DFT approaches with ECPs[1]. The purposes are to examine the performance of various density functionals on actinide species and to compare relativistic ECPs with DFT and "muffin-tin" with DFT.

The electronic structure of the actinide AnF_6 species has been the subject of numerous theoretical studies. The earlier studies using the Xα-scattered wave method, discrete variational-Xα method, as well as Hartree-Fock (HF) methods employing ECPs have been reviewed by Pepper and Bursten[2]. In recent years additional studies of UF_6[3] and NpF_6[4] have been reported using discrete variational-Xα methods. All-electron calculations on UF_6 have been carried out by deJong and Nieuwpoort[5] using the Dirac-Hartree-Fock approach and by Malli and Styszynski[6] using the Dirac-Fock-Breit approach.

In general, computation with density functional can obtain higher efficiency than that with other methods such as HF and Xα, etc. Moreover, DMol^3 has long been one of the fastest methods for molecular DFT calculations and can quickly perform structure optimizations of molecular and solid state systems using delocalized internal coordinates because DMol^3 is a unique density functional theory (DFT) quantum mechanical code. Owing to its unique approach to electrostatics, DMol^3 uses numerical functions on an atom-centered grid as its atomic basis[7]. It is a kind of tabulated basis[8]. The atomic basis functions are obtained from solution of the DFT equations for individual atoms and are stored as sets of cubic spline. Such basis sets are very accurate; the high quality of these basis sets minimizes superposition effects and consequently dissociation of molecules, for example, is accurately described. The long-range tail of the basis set exhibits correct charge distribution and allows an improved description of molecular polarizabilities. The electron density in DMol^3 is expanded in terms of multipolar partial densities. This provides a compact yet highly accurate representation of the density. The multipolar representation of the electron density is

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Received date: 2004-08-31

used to evaluate Coulomb potential via the solution of Poisson's equation. Thus calculation of the Coulomb potential, in principle a costly step, is replaced by fast evaluation of potential on each center, an operation which scales as N, N being the number of basis functions. The Hamiltonian matrix elements are calculated by using sophisticated numerical integration algorithm that scales close to order N when sparsity is taken into account. The algorithms in DMol^3 allow for very efficient parallelization of the numerical integration procedure. Simply, each processor performs numerical integration for a batch of grid points. After the task is completed, the contributions from various processors are combined, and the final DFT equation solved. The transition state search functionality can also be applied to both molecular and periodic system.

2 Calculation

Calculation was carried out on Pentium 4 2.0GHz with 512MB memory and 100G hard disk. The DMol^3 code which is packing in material studio is used as well as some density functionals in DMol^3: PWC, VWN,[9] PW91,[10] BP,[11] PBE,[12] BLYP,[13] BOP,[14] VWNBP,[6,8] RPBE,[15] and HCTH.[16] Meanwhile, both local density approximation (LDA) and generalized gradient approximation (GGA) are used.

3 Results and discussion

3.1 Geometric structure

The geometric structure of UF$_6$ is optimized by running DMol^3 code with various functional, basis sets, and approaches. All results show that the molecular structure belongs to Oh point group, see Fig.1. Comparing with experimental U-F bonding length (1.999 Å),[17] the minimum error of calculated results is 1.9%, while the maximum is 5.4%, which are listed in Table 1.

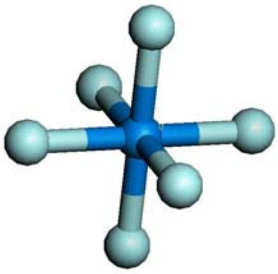

Fig.1 Geometric structure of UF$_6$.

Table 1 Comparison of calculated and experimental bonding lengths

	Functional	Basis sets	Bonding length(Å)	Error(%)
LDA	PWC	DND	2.03656	1.9
		DNP	2.03656	1.9
	VWN	DND	2.03619	1.9
		DNP	2.03619	1.9
GGA	PW91	DNP	2.07417	3.8
	BP	DNP	2.07803	4.0
	PBE	DNP	2.07533	3.8
	BLYP	DNP	2.10307	5.2
	BOP	DNP	2.10613	5.4
	VWNBP	DNP	2.07764	3.9
	RPBE	DNP	2.09063	4.6
	HCTH	DNP	2.07139	3.6

3.2 Vibrational frequencies

Vibrational frequencies of hexafluorides have been studied extensively in the gas phase and matrix spectroscopy. The early spectroscopy studies were reviewed by Weinstock and Goodman.[18] The vibrational frequencies calculated after the optimized geometry of UF$_6$ is summarized in Table 2. The results are also compared with experiments. The errors for each type of calculation are expressed with average absolute differences of all modes. The first three modes (v_1 through v_3) correspond to the U-F stretching modes and the modes v_4 through v_6 to the bending modes.

The calculated frequencies from the density functional approaches are much closer to the experimental ones. The average absolute errors are typically half as large as the Hatree-Fock results. The local density SVWN results are fairly close to experiments for the bending modes and are only slightly lower for the stretching modes. The v_3 bands are predicted to have frequency of 657cm^{-1}. The gradient corrected BLYP method predicts even lower values for the stretching modes (by 50—60cm^{-1} for the v_3 bands) and rather similar bending frequency. The hybrid B3LYP approach predicts somewhat higher frequency than BLYP. This result might be anticipated since the

Table 2 Comparison of calculated and experimental vibrational mode for UF_6 (cm^{-1})

UF_6 modes	$v_1(a_{1g})$	$v_2(e_g)$	$v_3(t_{1u})$	$v_4(t_{1u})$	$v_5(t_{2g})$	$v_6(t_{2u})$	Average absolute error
HF 6-31G*	761	582	702	209	216	157	45
SVWN 6-31G*	652	565	657	174	169	141	18
BLYP 6-31G*	598	517	605	175	158	135	29
B3LYP 6-31G*	653	552	647	191	178	150	14
B3LYP 6-31+G*	621	506	606	187	177	145	20
LDA PWC DND	558	550	558	180	180	114	36
LDA PWC DNP	558	550	558	180	180	115	36
LDA VWN DND	559	551	559	180	180	114	36
LDA VWN DNP	559	551	559	180	180	114	36
GGA PW91 DNP	520	511	520	177	177	113	56
GGA BP DNP	516	506	516	175	175	116	59
GGA PBE DNP	518	509	518	175	175	114	58
GGA BLYP DNP	505	492	505	168	168	119	67
GGA BOP DNP	498	486	498	170	170	123	69
GGA VWNBP DNP	516	506	516	175	175	116	59
GGA RPBE DNP	504	494	504	173	173	113	66
GGA HCTH DNP	499	487	499	181	181	114	66
Experimental[4]	667	534	626	186	200	143	

three-term B3LYP functional contains a component of exact Hartree-Fock exchange, and the HF results were uniformly high compared to experiments. The B3LYP value for the v_3 UF_6 bands is 647cm^{-1}. Overall SVWN and B3LYP results are in the best agreement with the observed vibrational frequencies.

Variations of the calculated frequencies for various methods correlate rather well with the predicted bond lengths. Hartree-Fock predicts a too long bond length and the frequencies are high; BLYP predicts a too long bond length and the frequencies are too low. SVWN and B3LYP predict bond lengths closer to experiments and the frequencies are also in better agreement.

Ordinary DFT (such as DFT in Gaussian) spend more over thirty times than DFT (LDA and GGA) in DMol^3. However, all errors resulting from performing GGA is bigger than Hartee-Fock method which was finished by GAUSSIAN 98w code and reported by Hay.[1] Meanwhile, the errors of LDA are better than those of Hartree-Fock, and they are still worse than ordinary DFT. Therefore, DMol^3 can be used in some large system, for instance, in the predication of properties and molecular structures of actinides or macro-molecules.

3.3 Thermodynamic parameters

After the molecular vibrational frequencies are obtained, some dynamic parameters of UF_6 can be calculated at 298.15K and 1×10^5Pa. The experimental entropy of UF_6 is 376.3±1.0 J/(K•mol), and the experimental heat capacity is 129.4±0.5 J/(K•mol).[19] The results listed in Table 3 show that the errors for entropy range from 13.9% to15.1%. Meanwhile, the maximum relative error for heat capacity is 7.3%, while the minimum is 4.8%. In addition, we can conclude that the results of LDA are better than those of GGA.

After testing, we have found that every calculation with DMol^3 spends less than 20 min, while the calculation with DFT in Gaussian 03W spends 90 min when using the same computer and operating system. It shows that DMol^3 is a code with a higher efficiency.

Table 3 The calculated values for some thermodynamic parameters of UF_6 and their errors (compared with experimental values)

Method	Functional	Basis sets	$S_{298.15\mathrm{K}}$ [J/(K•mol)]	Error(%)	$Cp_{298.15\mathrm{K}}$ [J/(K•mol)]	Error(%)
LDA	PWC	DND	428.61	13.9	135.69	4.9
		DNP	428.61	13.9	135.69	4.9
	VWN	DND	428.60	13.9	135.67	4.8
		DNP	428.60	13.9	135.67	4.8
GGA	PW91	DNP	431.46	14.7	137.73	6.4
	BP	DNP	431.17	14.6	137.90	6.6
	PBE	DNP	431.49	14.7	137.82	6.5
	BLYP	DNP	433.01	15.1	138.52	7.0
	BOP	DNP	432.17	14.8	138.81	7.3
	VWNBP	DNP	431.16	14.6	137.89	6.6
	RPBE	DNP	432.66	15.0	138.60	7.1
	HCTH	DNP	431.25	14.6	138.9	7.3

Acknowledgement

This work is supported by the Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics.

References

1 Hay P J, Martin R L J. Chem Phys, 1998, **109**(8): 3875

2 Pepper M, Bursten B E. Chem Rev, 1991, **91**: 719

3 Onoe J, Takeuchi K, Mukoyama T *et al*. J Chem Phys, 1993, **99**: 6810

4 Kaltsoyannis N, Bursten B E. Inorg Chem, 1995, **99**: 17085

5 deJong W A, Niewspoon W C. Int J Quantum Chem, 1996, **58**: 203

6 Malli G I, Styszynski J. J Chem Phys, 1996, **104**: 1012

7 Delley B. J Chem Phys, 2000, **113**: 7756

8 Delley B. J Chem Phys, 1990, **92**: 508

9 Vosko S J, Wilk L, Nusair M. Can J Phys, 1980, **58**: 1200-1211

10 Perdew J P, Wang Y. Phys Rev, 1992, **B45**: 13244

11 Becke A D. J Chem Phys, 1988, **88**: 2547; Perdew J P, Wang Y. Phys Rev, 1992, **B45**: 13244

12 Perdew J P, Burke K, Ernzerhof M. Phys Rev Lett, 1996, **77**: 3865

13 Lee C, Yang W, Parr R G. Phys Rev B, 1988, **37**: 786

14 Tsuneda Takao, Suzumura Toshihisa, Hirao Kimihiko. J Chem Phys, 1999, **110**(33): 10664

15 Hammer B, Hansen LB, Norskov J K. Phys Rev, 1999, **B 59**: 7413

16 Boese A D, Handy N C. J Chem Phys, 2001, **114**: 5497

17 Seip H M. Acta Chem Scand, 1965, **20**: 2698

18 Weinstock B, Goodman G L. Adv Chem Phys, 1965, **9**: 169

19 Guilaumont R, Fanghänel T, Fuger J *et al*. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. Elsevier, 2003