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二阶多参考态微扰理论计算电子亲和势

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摘要: 采用二阶多参考态微扰理论计算了F, Cl, OH, SH, CN, CH₂和NH₂的电子亲和势. 另外, 还考察了基函数和完全活性空间大小对电子亲和势精度的影响. 通过和CASSCF, CASPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP和B2PLYP的计算结果比较发现, 针对目前所用的基函数, 二阶多参考态微扰理论的总体计算效果是最好的.

关键词: 电子亲和势; 多参考态微扰理论; 基函数; 完全活性空间
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Computation of Electron Affinities with the Second Order Multireference Perturbation Theory

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Abstract: Electron affinities of F, Cl, OH, SH, CN, CH₂, and NH₂ have been computed with the second order multireference perturbation theory. The effects of basis set and size of the complete active space on accuracy of electron affinity have also been investigated. The results are compared with calculations performed with CASSCF, CASPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP. The overall performance of the second order multireference perturbation theory is best at the level of basis sets used in this study.

Key Words: Electron affinity; Multireference perturbation theory; Basis set; Complete active space

1 Introduction

Koopmans' theorem¹ provides one simple approach to calculate theoretically the electron affinity (EA) at the Hartree-Fock level. However, due to the neglect of relaxation in Koopmans' theorem, the computed EA value at this level tends to be too small in comparison with the experimental data. To deal with this problem it is chosen to calculate the energies of a neutral species and its negative ion separately and take the difference as the EA. But it turns out that computing this difference is much challenging for computation chemistry, which requires a balanced description of both the neutral system and anion.

Since the anion has one more electron than its neutral counterpart its correlation energy is also larger than that of the latter. Therefore, a post Hartree-Fock calculation should be performed for obtaining an accurate EA value. The term "accurate" here will imply agreement with experiment to 0.1 eV or better. However, this level of accuracy has been proven to be very difficult to achieve.

Density functional theory has been widely used to calculate the electron affinity as well as other properties of molecular systems,^{2–10} its accuracy depends on the basis set and the density functional used in the study. Multireference perturbation

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theory is one of the important methods beyond the Hartree-Fock approximation. It combines the static and dynamic correlation effects into one single framework and provides versatile ways to describe the electronic structures of atomic and molecular systems. There are many research works on this field.^{11–40} To list just a few, there are Hylleraas variational perturbation theory by Cave and Davidson,¹¹ CASPT2 and CASPT3,¹² multireference Møller-Plesset perturbation theory of Hirao,^{13,14} multireference open-shell perturbation theory of Kozłowski and Davidson,^{15,16} the second order generalized van Vleck perturbation theory of Hoffmann *et al.*,^{17,19} the state-specific multireference perturbation theory of Mukherjee *et al.*,¹⁸ the configuration-based multireference second order perturbation theory of Wen *et al.*,^{20,36} the n -electron valence state perturbation theory of Angeli *et al.*,^{21,22} the multireference perturbation theory of Chen *et al.*,²³ the multiconfiguration perturbation theory of Surján *et al.*,^{24,25,32} the valence bond perturbation theory of Wu *et al.*,^{29,40} a spin adapted size extensive state specific multireference perturbation theory of Liu *et al.*,^{33,34} the orbitally invariant multireference perturbation theory of Chen and Hoffmann,³⁵ the block correlated perturbation theory of Xu and Li,³⁷ the size extensive multireference perturbation theory of Chen and Fan,³⁸ and SDS-MS-MRPT2 by Liu and Hoffmann.³⁹ In spite of substantial works on the perturbation theory as shown above, their applications to electron affinity problems are not as many as one may expect.

In this study, we will compute the electron affinities of F, Cl, CN, OH, SH, CH₂, and NH₂ with the second order multireference perturbation theory.²³ Comparisons with the complete active space self-consistent field (CASSCF),⁴¹ CASPT2,¹² the coupled cluster with single and double excitations (CCSD),^{42–45} CCSD plus the perturbation correction of triple excitations (CCSD(T)),⁴⁶ and density functional theories such as B3LYP,^{47–49} X3LYP,⁵⁰ M06,⁵¹ HTCH,⁵² TPSS,⁵³ B97D3,⁵⁴ mPW2PLYP,⁵⁵ and B2PLYP,⁵⁶ will be made to show their different performances. Especially, the effects of basis sets and size of the reference spaces on EA will be investigated and discussed in details.

2 Computational method

The second and third order multireference perturbation expressions can be written as follows^{1,23}

$$E_p = \varepsilon_p^{(0)} + \sum_{i,j \leq n} \sum_{a>n} \frac{u_p^{(0)}(i) H_{ia} H_{aj} u_p^{(0)}(j)}{\varepsilon_p^{(0)} - H_{aa}} \lambda^2 + \sum_{i,j \leq n} \sum_{\substack{a,b>n \\ a \neq b}} \frac{u_p^{(0)}(i) H_{ia} H_{ab} H_{bj} u_p^{(0)}(j)}{(\varepsilon_p^{(0)} - H_{aa})(\varepsilon_p^{(0)} - H_{bb})} \lambda^3 + \dots \quad (1)$$

where $\varepsilon_p^{(0)}$ is the p -th eigenvalue and $u_p^{(0)}(i)$ is the i -th component of the corresponding p -th eigenvector in the reference space. The dimension of the reference space is n . H_{ij} is the Hamiltonian matrix element with respect to the i -th and j -th configuration functions. λ is a perturbation parameter and is set

equal to unity for the final energy E_p . For an efficient implementation, Eq.(1) can be further expressed as

$$E_p = \varepsilon_p^{(0)} + \sum_{a>n} \frac{\bar{H}_{pa} \bar{H}_{ap}}{\varepsilon_p^{(0)} - H_{aa}} \lambda^2 + \sum_{a>n} \sum_{\substack{b>n \\ a \neq b}} \frac{\bar{H}_{pa} H_{ab} \bar{H}_{bp}}{(\varepsilon_p^{(0)} - H_{aa})(\varepsilon_p^{(0)} - H_{bb})} \lambda^3 + \dots \quad (2)$$

with $\bar{H}_{pa}$ defined as

$$\bar{H}_{pa} = \sum_{i=1}^n u_p^{(0)}(i) H_{ia} \quad (3)$$

Eq.(2) is to some extent formally similar to the single reference perturbation expressions.^{1,23} But the key differences lie in the expression of $\bar{H}_{pa}$ to which not only the p -th state but also other states within the reference space have contributions to the energy E_p .

The electron affinities of F, Cl, OH, CN, SH, CH₂, and NH₂ are calculated with the above second order multireference perturbation theory (MRPT2). Different basis sets with varieties of levels of theoretical methods have been exploited to calculate the electron affinity in literature. In order to compare the performance of different methods conveniently, the system basis sets, Dunning's correlation consistent basis functions,^{57,58} cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ are used for all theoretical approaches in the present work. CASSCF wave function is chosen as the zeroth order wavefunction in MRPT2 and is calculated with GAMESS.⁵⁹ CAS(N,M) means that the configuration space is constructed with N electrons distributed among M orbitals in all possible ways. Calculations with CCSD, CCSD(T), B3LYP, X3LYP, M06, HTCH, TPSS, B97D3, mPW2PLYP, and B2PLYP are carried out with Gaussian program.⁶⁰ Calculations with CASPT2 are carried out with MOLPRO.⁶¹

3 Results and discussion

3.1 Electron affinities of F and Cl

There are many theoretical works on the electron affinity (EA) of F. Here only some representative works are discussed. They are the fourth order Møller-Plesset perturbation theory (MP4) and the coupled cluster theory,⁶² Gaussian-1 theory,⁶³ Gaussian-2 theory,⁶⁵ BLYP density functional theory,⁶⁶ one electron propagator,^{67,68} and the multireference coupled cluster theory.⁶⁹ In comparison with the EA value of 3.65 eV calculated with MP4,⁶² the coupled cluster result (3.37 eV) is much close to the experimental result of 3.401 eV.⁶⁴ The theoretical estimation of Pople *et al.*⁶⁵ for the affinity 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. The EA values (3.550 eV⁶⁷ and 3.538 eV⁶⁸) calculated with one electron propagator theories are overestimated. The results calculated with the multireference coupled cluster theory at the basis level of aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ are 3.2378, 3.4014, and 3.4986 eV, respectively.⁶⁹ These results are presented at the bottom of Table 1 for the convenience of comparison.

Table 1 Electron affinities (EA) of F calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(F)/(a.u.)$	$E(F^-)/(a.u.)$	EA/eV
cc-pVDZ	CASSCF	-99.429375	-99.451621	0.605
	CASPT2	-99.520037	-99.551177	0.847
	MRPT2	-99.533222	-99.566845	0.915
	CCSD	-99.526690	-99.557846	0.848
	CCSD(T)	-99.527574	-99.558453	0.840
	B3LYP	-99.726600	-99.769792	1.175
	X3LYP	-99.698900	-99.739480	1.104
	M06	-99.695328	-99.747367	1.416
	HCTH	-99.694183	-99.745557	1.398
	TPSS	-99.731401	-99.769522	1.037
	B97D3	-99.675702	-99.720999	1.233
	mPW2PLYP	-99.662265	-99.700045	1.028
	B2PLYP	-99.660923	-99.699124	1.040
cc-pVTZ	CASSCF	-99.462487	-99.522939	1.645
	CASPT2	-99.608776	-99.685635	2.091
	MRPT2	-99.629778	-99.713493	2.278
	CCSD	-99.616771	-99.692820	2.069
	CCSD(T)	-99.620361	-99.698384	2.123
	B3LYP	-99.762866	-99.850177	2.376
	X3LYP	-99.735270	-99.819880	2.302
	M06	-99.722897	-99.809492	2.356
	HCTH	-99.729265	-99.822278	2.531
	TPSS	-99.766051	-99.848561	2.245
	B97D3	-99.711790	-99.799662	2.391
	mPW2PLYP	-99.712213	-99.793720	2.218
	B2PLYP	-99.712143	-99.794945	2.253
aug-cc-pVDZ	CASSCF	-99.434409	-99.534289	2.718
	CASPT2	-99.540953	-99.657753	3.178
	MRPT2	-99.555382	-99.682400	3.456
	CCSD	-99.547749	-99.662690	3.128
	CCSD(T)	-99.550069	-99.668634	3.226
	B3LYP	-99.739496	-99.870373	3.562
	X3LYP	-99.711950	-99.840520	3.498
	M06	-99.706058	-99.833058	3.456
	HCTH	-99.707343	-99.849552	3.870
	TPSS	-99.743769	-99.870716	3.454
	B97D3	-99.688316	-99.822075	3.640
	mPW2PLYP	-99.676727	-99.801479	3.395
	B2PLYP	-99.675638	-99.802108	3.441
Exp. ⁶⁴				3.401
Adamowicz <i>et al.</i> ⁶²				3.653, 3.373 ^a
Pople <i>et al.</i> ⁶³				3.46
Curtiss <i>et al.</i> ⁶⁵				3.48
Gill <i>et al.</i> ⁶⁶				3.42
Yeager <i>et al.</i> ⁶⁷				3.550
Ortiz ⁶⁸				3.538
Jana <i>et al.</i> ⁶⁹				3.372

^a3.653 and 3.373 eV were calculated respectively with the fourth order perturbation theory and coupled cluster theory. The complete active spaces for F and F⁻ are CAS(5,7) and CAS(6,7), respectively.

In this study, the complete active spaces for F and F⁻ are CAS(5,7) and CAS(6,7), respectively. The electron affinities calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HTCH, TPSS, B97D3, mPW2PLYP, and B2PLYP are listed in Table 1. As can be seen from the table, the EA values calculated with the cc-pVDZ basis set are far away from the experimental value of 3.401 eV⁶⁴ in spite of various theoretical methods used. As the basis set is increased to cc-pVTZ, the number of the bases is changed from 14 to 30. Yet the computed EAs are still not so close to the experimental value although they are improved substantially. However, when aug-cc-pVDZ is considered, the theoretical EA values computed with MRPT2, CCSD, CCSD(T), and CASPT2 become much closer to the experimental result in spite of the fact that the number of the bases in the aug-cc-pVDZ is less than the number of the bases in the cc-pVTZ. This demonstrates the important role of diffuse functions in obtaining accurate theoretical EA values. Among the wavefunction methods, the best agreement with the experimental EA value of 3.401 eV⁶⁴ has been achieved by MRPT2/aug-cc-pVDZ with the difference less than 0.100 eV. CASPT2 results are less accurate than the results of MRPT2 and CCSD(T) but are slightly better than the results of CCSD for this problem at the level of aug-cc-pVDZ. However, all CASSCF results are not satisfactory and their differences with the experimental value of 3.401 eV⁶⁴ are still as large as about 0.700 eV even at the level of aug-cc-pVDZ. The accuracies of M06, TPSS, mPW2PLYP, and B2PLYP are comparable to the accuracy of MRPT2 and are better than the accuracies of B3LYP, X3LYP, HTCH, and B97D3. In comparison with the B3LYP results, Gill *et al.*⁶⁶ obtained an accurate EA value of 3.42 eV for F with BLYP/6-311+G(2df, p) as shown at the bottom of Table 1, but results of BLYP are not stable and case dependent. This is the nature of density functional theory as will be shown later.

Because of similarity of the valence electron structure between Cl and F, the complete active spaces for Cl and Cl⁻ are also CAS(5,7) and CAS(6,7), the same as for F and F⁻, respectively. The calculated electron affinities of Cl with various methods are listed in Table 2. It can be seen from the table that the best EA value is 3.601 eV obtained with MRPT2/aug-cc-pVDZ, which is comparable to the accuracy achieved with the renormalized electron propagator method at the level of aug-cc-pVTZ by Ortiz⁶⁸ as shown at the bottom of the table. The EA value of 3.617 eV with a model potential-quantum Monte Carlo study⁷⁰ is in very good agreement with experiment,⁷¹ yet its error is as high as ± 0.198 eV because of stochastic nature of Monte Carlo method. Among the density functional theories, the accuracies of mPW2PLYP and B2PLYP are comparable to the accuracy of MRPT2. Their performances are better than that of CCSD, CCSD(T), CASPT2, and other density functional methods presented in Table 2. The accuracy of CASSCF results at different levels of basis sets are still inferior to the ac-

curacies of other methods listed in the table indicating the important role played by the dynamic correlation.

3.2 Electron affinities of OH and SH

The experimental equilibrium bond lengths of OH and OH⁻⁷² are used for electron affinity calculation. OH is an isoelectronic system of F. However, its electronic structure seems more complicated than the latter. We first explore the complete active space CAS(5,6) and CAS(6,6) for OH and OH⁻ separately. As shown at the top of Table 3, except the positive EA value calculated with MRPT2/cc-pVDZ, all other methods, CASSCF, CASPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HTCH, TPSS, B97D3, mPW2PLYP, and B2PLYP at the same basis, predict negative EA values indicating that OH⁻ is not stable, which is however not in agreement with the experimental observation.⁷³ Furthermore, CASSCF wavefunction at cc-pVTZ basis still produces a negative EA value. These calculations demonstrate the difficulty in obtaining the electron affinity of OH. As the basis set is extended to aug-cc-pVDZ, EAs calculated with various methods except CASSCF are improved substantially. However, the CASPT2, CCSD, and CCSD(T) results still underestimate the experimental value while the MRPT2 result overestimates it. As the basis is extended further to aug-cc-pVTZ, the EAs calculated with CASPT2, CCSD, and CCSD(T) are improved as shown in the lower part of Table 3. However, the change of the basis set almost has no effect on the results of CASSCF and MRPT2, which means that a large static correlation may be needed for a further improvement on their EA values. Therefore, the complete active spaces are enlarged from CAS(5,6) and CAS(6,6) to CAS(7,7) and CAS(8,7) for OH and OH⁻, respectively. The corresponding results are listed at the lower part of Table 3. The MRPT2 result of 1.91 eV becomes better than the result of 2.044 eV obtained with a small complete active space and agrees very well with the experimental value of 1.83 eV⁷³ to within 0.10 eV. However, the CASSCF and CASPT2 results are still not satisfactory. The EA value of 1.78 eV calculated with MP4 and a large basis 6-311++G(3df, 3pd) is reported by Frenking and Koch⁷⁵ and are in very good agreement with the experimental value of 1.83 eV. Though partial quadruple excitations in MP4 have been included in CASPT2, yet it seems that these excitations are still not enough to achieve an accurate result with CASPT2.

Among the density functional methods, the results of B3LYP, X3LYP, B97D3, mPW2PLYP, and B2PLYP at the level of aug-cc-pVTZ are in very close agreement with the experimental value of 1.83 eV.⁷³ Similar results of other density function theories like BLYP^{66,74} are listed at the bottom of Table 3.^{65–68,73–75} As can be seen from the results of Tables 1–3, density functional theories as a whole are reliable approaches at a very large basis set though the performance of each individual functional is different from each other and is dependent on the system studied.

Table 2 Electron affinities of Cl calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{Cl})/(\text{a.u.})$	$E(\text{Cl}^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF	-459.487049	-459.573113	2.342
	CASPT2	-459.586003	-459.676216	2.455
	MRPT2	-459.619926	-459.711673	2.497
	CCSD	-459.597739	-459.688435	2.468
	CCSD(T)	-459.598893	-459.689586	2.468
	B3LYP	-460.158464	-460.266576	2.942
	X3LYP	-460.109200	-460.215200	2.884
	M06	-460.124069	-460.237609	3.090
	HCTH	-460.206465	-460.317992	3.035
	TPSS	-460.160420	-460.267922	2.925
	B97D3	-460.169267	-460.274525	2.864
	mPW2PLYP	-460.013773	-460.115653	2.772
	B2PLYP	-459.999667	-460.101273	2.765
cc-pVTZ	CASSCF	-459.508674	-459.599707	2.477
	CASPT2	-459.644878	-459.757529	3.065
	MRPT2	-459.713019	-459.828584	3.145
	CCSD	-459.666282	-459.778021	3.041
	CCSD(T)	-459.671808	-459.785130	3.084
	B3LYP	-460.174662	-460.297536	3.344
	X3LYP	-460.125500	-460.246300	3.288
	M06	-460.135280	-460.258112	3.342
	HCTH	-460.221673	-460.345835	3.379
	TPSS	-460.176774	-460.297527	3.286
	B97D3	-460.185880	-460.305288	3.249
	mPW2PLYP	-460.042919	-460.161176	3.218
	B2PLYP	-460.030020	-460.148400	3.221
aug-cc-pVDZ	CASSCF	-459.489136	-459.600495	3.030
	CASPT2	-459.598382	-459.720792	3.331
	MRPT2	-459.633432	-459.765752	3.601
	CCSD	-459.609931	-459.734186	3.381
	CCSD(T)	-459.612222	-459.738302	3.431
	B3LYP	-460.161471	-460.298160	3.720
	X3LYP	-460.112400	-460.247400	3.674
	M06	-460.126265	-460.264790	3.769
	HCTH	-460.209578	-460.349847	3.817
	TPSS	-460.162675	-460.296231	3.634
	B97D3	-460.172078	-460.305836	3.640
	mPW2PLYP	-460.019400	-460.151471	3.594
	B2PLYP	-460.005489	-460.137444	3.591
	Exp. ⁷¹			3.615
	Curtiss <i>et al.</i> ⁶⁵			3.60
	Ortiz ⁶⁸			3.613
	Yoshida <i>et al.</i> ⁷⁰			3.617

The complete active spaces for Cl and Cl⁻ are CAS(5,7) and CAS(6,7), respectively.

Table 3 Electron affinities of OH calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{OH})/(\text{a.u.})$	$E(\text{OH}^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF*	-75.442468	-75.360601	-2.228
	CASPT2*	-75.549612	-75.527012	-0.615
	MRPT2*	-75.566923	-75.571652	0.129
	CCSD	-75.557537	-75.532992	-0.668
	CCSD(T)	-75.559266	-75.535270	-0.653
	B3LYP	-75.731924	-75.721026	-0.297
	X3LYP	-75.704780	-75.691470	-0.362
	M06	-75.695447	-75.689386	-0.165
	HCTH	-75.711443	-75.706846	-0.125
	TPSS	-75.738045	-75.723111	-0.406
	B97D3	-75.688642	-75.678700	-0.271
	mPW2PLYP	-75.669485	-75.652901	-0.451
	B2PLYP	-75.669241	-75.653042	-0.441
cc-pVTZ	CASSCF*	-75.469812	-75.413562	-1.531
	CASPT2*	-75.626530	-75.647583	0.573
	MRPT2*	-75.647369	-75.698814	1.400
	CCSD	-75.632632	-75.649877	0.469
	CCSD(T)	-75.637722	-75.657692	0.543
	B3LYP	-75.764105	-75.790402	0.716
	X3LYP	-75.737070	-75.76086	0.647
	M06	-75.721466	-75.746763	0.688
	HCTH	-75.742230	-75.772215	0.816
	TPSS	-75.768223	-75.790173	0.597
	B97D3	-75.720105	-75.746275	0.712
	mPW2PLYP	-75.712958	-75.734889	0.597
	B2PLYP	-75.713849	-75.736983	0.629
aug-cc-pVDZ	CASSCF*	-75.454418	-75.457839	0.093
	CASPT2*	-75.573022	-75.628419	1.507
	MRPT2*	-75.590455	-75.665554	2.044
	CCSD	-75.580634	-75.635832	1.502
	CCSD(T)	-75.583992	-75.643882	1.630
	B3LYP	-75.748921	-75.816934	1.851
	X3LYP	-75.722000	-75.78785	1.792
	M06	-75.710374	-75.773186	1.709
	HCTH	-75.728804	-75.806155	2.105
	TPSS	-75.754002	-75.817795	1.736
	B97D3	-75.705246	-75.775367	1.908
	mPW2PLYP	-75.687914	-75.752148	1.748
	B2PLYP	-75.687852	-75.753854	1.796
aug-cc-pVTZ	CASSCF*	-75.472903	-75.475076	0.059
	CASPT2*	-75.632772	-75.692257	1.619
	MRPT2*	-75.650849	-75.727345	2.082
	CCSD	-75.639697	-75.696999	1.559
	CCSD(T)	-75.645575	-75.709421	1.737
	B3LYP	-75.768563	-75.836237	1.841
	X3LYP	-75.741650	-75.807110	1.781
	M06	-75.724825	-75.787695	1.711
	HCTH	-75.747830	-75.824679	2.091
	TPSS	-75.772660	-75.835850	1.719

to be continued

continued Table 3

Basis set	Method	$E(\text{OH})/(\text{a.u.})$	$E(\text{OH}^-)/(\text{a.u.})$	EA/eV
aug-cc-pVDZ	B97D3	-75.724778	-75.794180	1.886
	mPW2PLYP	-75.718333	-75.783504	1.773
	B2PLYP	-75.719262	-75.786403	1.827
	CASSCF**	-75.476469	-75.481469	0.136
	CASPT2**	-75.631985	-75.691580	1.622
	MRPT2**	-75.587459	-75.657657	1.910
Exp. ⁷³				1.83
Curtiss <i>et al.</i> ⁶⁵				1.87
Gill <i>et al.</i> ⁶⁶				1.72
Yeager <i>et al.</i> ⁶⁷				1.68
Ortiz ⁶⁸				1.85
Proft <i>et al.</i> ⁷⁴				1.85
Frenking ⁷⁵				1.78

*The complete active spaces for OH and OH⁻ are CAS(5,6) and CAS(6,6), respectively.

**The complete active spaces for OH and OH⁻ are CAS(7,7) and CAS(8,7), respectively.

The bond lengths of SH and SH⁻ are 0.1338 and 0.1342 nm,⁶⁸ respectively. They are optimized with the second-order Møller-Plesset perturbation theory at the level of 6-311++G(*d,p*) basis. Electron affinities of SH calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP are presented in Table 4. In comparison with the results of OH in Table 3, EAs of SH are all positive at the level of cc-pVDZ basis, which indicates that EAs of SH are easier to be calculated. At the level of aug-cc-pVDZ, the results of MRPT2, B3LYP, X3LYP, M06, TPSS, B97D3, mPW2PLYP, and B2PLYP are very close to the experimental value of 2.319 eV.⁷⁶ As the basis set is extended to aug-cc-pVTZ, the CCSD(T) result is also improved and is in close agreement with the experimental result. But the CASPT2 and CCSD results are still about 0.2 eV less than the experimental value. The performance of CASSCF even with the aug-cc-pVTZ basis is still much inferior to the performances of all other methods listed in the table.

3.3 Electron affinity of CN

The experimental equilibrium bond lengths of CN and CN⁻ are separately 0.1172 and 0.1177 nm⁷² and are exploited for computation of the electron affinity. The complete active spaces for CN and CN⁻ are CAS(7,7) and CAS(8,7), respectively. The results calculated with various theoretical methods are presented in Table 5. In comparison with the experimental EA value of 3.82 eV,⁷⁷ the performances of MRPT2, HCTH, M06, and B2PLYP with aug-cc-pVDZ are better than those of other theoretical approaches presented in the table.

The previous studies on the electron affinity of CN are listed at the bottom of the table for the purpose of comparison. Among them, the results of Gaussian-2 theory by Pople *et al.*⁶⁵ and one electron propagator method by Ortiz⁶⁸ are very close to the experimental value of 3.82 eV.⁷⁷ However, the BLYP density functional theory result by Gill *et al.*⁶⁶ is inferior to the BLYP result by Proft and Geerlings⁷⁴ due to their different basis sets used in the study. The EA value predicted by Yeager *et al.*⁶⁷

with the electron propagator method is also not satisfactory.

3.4 Electron affinities of CH₂ and NH₂

The geometrical parameters of CH₂, CH₂⁻, NH₂, and NH₂⁻ are taken from references,^{68,78} respectively. Electron affinities of CH₂ and NH₂ are presented in Tables 6 and 7.^{65-68,74,78-82} As can be seen from these two tables, most of EA values of CH₂ and NH₂ are negative at the basis levels of cc-pVDZ and cc-pVTZ. Even though the EAs of CH₂ calculated with MRPT2 and density functional methods at the level of cc-pVTZ are positive, yet their absolute errors with the experimental value of 0.652 eV⁷⁹ are still large. These results demonstrate that CH₂ and NH₂ are more difficult to describe than OH as discussed in Section 3.2. As the basis is extended to aug-cc-pVDZ, the EAs of CH₂ calculated with all theoretical approaches are improved substantially and are listed in the lower part of Table 6. The MRPT2 result of CH₂ is in very close agreement with the experimental value with the absolute error less than 0.04 eV.⁷⁹ On the other hand, the EA of NH₂ calculated with MRPT2/aug-cc-pVDZ is still not satisfactory, which is similar to the situation of OH in Table 3. Therefore, the complete active spaces of NH₂ and NH₂⁻ are enlarged from CAS(6,6) and CAS(7,6) to CAS(7,7) and CAS(8,7), respectively. As can be seen from Table 7, the effect of the size of the complete active space on EA values is very significant. The absolute error of the MRPT2 result is only 0.005 eV in comparison with the experimental value of 0.77 eV.⁸¹ The performances of CASSCF and CASPT2 are still not satisfactory.

Similar to the results of OH in Table 3, B3LYP, X3LYP, and B97D3 demonstrate very good performances for both CH₂ and NH₂. The EA values of CH₂ calculated with HCTH, mPW2PLYP, and B2PLYP at the level of aug-cc-pVDZ is also in good agreement with the experimental result.⁷⁹ It is worthy to mention that good accuracies have been achieved with Gaussian-2 theory⁶⁵, density functional theory,^{66,74} one electron propagator method,⁶⁸ and the multireference configuration interaction method,^{80,82} as listed at the bottoms of Tables 6 and 7.

Table 4 Electron affinities of SH calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{SH})/(\text{a.u.})$	$E(\text{SH}^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF	-398.108697	-398.128461	0.538
	CASPT2	-398.210130	-398.248650	1.048
	MRPT2	-398.235440	-398.282653	1.285
	CCSD	-398.222340	-398.262482	1.092
	CCSD(T)	-398.224540	-398.264982	1.100
	B3LYP	-398.762179	-398.818561	1.534
	X3LYP	-398.713300	-398.767600	1.478
	M06	-398.724839	-398.784399	1.621
	HCTH	-398.800444	-398.859615	1.610
	TPSS	-398.764711	-398.821182	1.537
	B97D3	-398.758832	-398.812701	1.466
	mPW2PLYP	-398.616067	-398.666134	1.362
	B2PLYP	-398.603216	-398.653117	1.358
aug-cc-pVDZ	CASSCF	-398.117909	-398.154627	0.999
	CASPT2	-398.222273	-398.296418	2.018
	MRPT2	-398.245210	-398.330519	2.321
	CCSD	-398.234393	-398.309921	2.055
	CCSD(T)	-398.237757	-398.315668	2.120
	B3LYP	-398.766652	-398.853388	2.360
	X3LYP	-398.717900	-398.803000	2.316
	M06	-398.728621	-398.815648	2.368
	HCTH	-398.804985	-398.894789	2.444
	TPSS	-398.768252	-398.852163	2.283
	B97D3	-398.763062	-398.847519	2.298
	mPW2PLYP	-398.622755	-398.705080	2.240
	B2PLYP	-398.610042	-398.692367	2.240
aug-cc-pVTZ	CASSCF	-398.123164	-398.167095	1.195
	CASPT2	-398.270893	-398.348337	2.107
	MRPT2	-398.298175	-398.383980	2.335
	CCSD	-398.284684	-398.363169	2.136
	CCSD(T)	-398.291363	-398.373493	2.235
	B3LYP	-398.781207	-398.867099	2.337
	X3LYP	-398.732500	-398.816700	2.292
	M06	-398.739226	-398.821966	2.251
	HCTH	-398.818271	-398.907665	2.433
	TPSS	-398.783921	-398.866747	2.254
	B97D3	-398.778490	-398.861567	2.261
	mPW2PLYP	-398.646459	-398.729204	2.252
	B2PLYP	-398.634601	-398.717551	2.257
Exp. ⁷⁶				2.319
Curtiss <i>et al.</i> ⁶⁵				2.30
Ortiz ⁶⁸				2.29
Proft <i>et al.</i> ⁷⁴				2.27

The complete active spaces for SH and SH⁻ are CAS(5,6) and CAS(6,6), respectively.

Table 5 Electron affinity values for CN($X^2\Sigma^-$) calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{CN})/(\text{a.u.})$	$E(\text{CN}^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF	-92.335867	-92.413301	2.107
	CASPT2	-92.473924	-92.572488	2.682
	MRPT2	-92.489766	-92.597552	2.933
	CCSD	-92.476679	-92.580602	2.828
	CCSD(T)	-92.489071	-92.592053	2.802
	B3LYP	-92.719427	-92.836492	3.186
	X3LYP	-92.680140	-92.795650	3.143
	M06	-92.656898	-92.772010	3.132
	HCTH	-92.703971	-92.811440	2.924
	TPSS	-92.742323	-92.849176	2.908
	B97D3	-92.665532	-92.771210	2.876
	mPW2PLYP	-92.636027	-92.748604	3.063
	B2PLYP	-92.638959	-92.749682	3.013
cc-pVTZ	CASSCF	-92.357154	-92.447637	2.462
	CASPT2	-92.548498	-92.670695	3.325
	MRPT2	-92.565941	-92.697747	3.587
	CCSD	-92.547224	-92.675723	3.497
	CCSD(T)	-92.565704	-92.694000	3.491
	B3LYP	-92.745622	-92.882172	3.716
	X3LYP	-92.706420	-92.841510	3.676
	M06	-92.682730	-92.812113	3.521
	HCTH	-92.724858	-92.850691	3.424
	TPSS	-92.765545	-92.890455	3.399
	B97D3	-92.689034	-92.813643	3.391
	mPW2PLYP	-92.675186	-92.808240	3.621
	B2PLYP	-92.679296	-92.810876	3.580
aug-cc-pVDZ	CASSCF	-92.339570	-92.437903	2.676
	CASPT2	-92.486413	-92.616759	3.547
	MRPT2	-92.498063	-92.636016	3.754
	CCSD	-92.488563	-92.624561	3.701
	CCSD(T)	-92.502297	-92.639388	3.730
	B3LYP	-92.725050	-92.873580	4.042
	X3LYP	-92.68593	-92.833310	4.010
	M06	-92.661954	-92.804506	3.879
	HCTH	-92.709121	-92.849447	3.818
	TPSS	-92.747030	-92.882847	3.696
	B97D3	-92.670371	-92.807576	3.734
	mPW2PLYP	-92.643524	-92.788060	3.933
	B2PLYP	-92.646497	-92.789344	3.887
Exp. ⁷⁷ Curtiss <i>et al.</i> ⁶⁵ Gill <i>et al.</i> ⁶⁶ Yeager <i>et al.</i> ⁶⁷ Ortiz ⁶⁸ Proft <i>et al.</i> ⁷⁴				3.82
				3.97
				4.58
				4.13
				3.83
				3.75

The complete active spaces for CN and CN⁻ are CAS(7,7) and CAS(8,7), respectively.

Table 6 Electron affinities for CH₂ (X^3B_1) calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{CH}_2)/(\text{a.u.})$	$E(\text{CH}_2^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF	-38.959891	-38.899932	-1.632
	CASPT2	-39.032521	-39.003184	-0.798
	MRPT2	-39.044488	-39.026679	-0.485
	CCSD	-39.039718	-39.014525	-0.686
	CCSD(T)	-39.041443	-39.017528	-0.651
	B3LYP	-39.153277	-39.145220	-0.219
	X3LYP	-39.130220	-39.120080	-0.276
	M06	-39.116865	-39.103650	-0.360
	HCTH	-39.159379	-39.149233	-0.276
	TPSS	-39.166753	-39.151923	-0.404
	B97D3	-39.126170	-39.116682	-0.258
	mPW2PLYP	-39.104973	-39.088795	-0.440
	B2PLYP	-39.104830	-39.088783	-0.437
cc-pVTZ	CASSCF	-38.970892	-38.922769	-1.310
	CASPT2	-39.068241	-39.061653	-0.179
	MRPT2	-39.080086	-39.088020	0.216
	CCSD	-39.074460	-39.071221	-0.088
	CCSD(T)	-39.077853	-39.077433	-0.011
	B3LYP	-39.168706	-39.177582	0.242
	X3LYP	-39.145670	-39.152510	0.186
	M06	-39.131244	-39.134280	0.083
	HCTH	-39.172728	-39.177577	0.132
	TPSS	-39.179626	-39.180900	0.035
	B97D3	-39.141400	-39.147786	0.174
	mPW2PLYP	-39.125402	-39.127586	0.059
	B2PLYP	-39.125854	-39.128549	0.073
aug-cc-pVDZ	CASSCF	-38.961275	-38.926716	-0.940
	CASPT2	-39.038795	-39.048415	0.262
	MRPT2	-39.047047	-39.069572	0.613
	CCSD	-39.045787	-39.059058	0.361
	CCSD(T)	-39.048037	-39.064910	0.459
	B3LYP	-39.157485	-39.185323	0.758
	X3LYP	-39.134520	-39.160560	0.709
	M06	-39.120375	-39.140653	0.552
	HCTH	-39.164496	-39.190814	0.717
	TPSS	-39.170160	-39.188804	0.507
	B97D3	-39.130612	-39.156568	0.706
	mPW2PLYP	-39.109371	-39.129833	0.557
	B2PLYP	-39.109269	-39.130302	0.572
Exp. ⁷⁹				0.652
Noro <i>et al.</i> ⁷⁸				0.60
Curtiss <i>et al.</i> ⁶⁵				0.66
Gill <i>et al.</i> ⁶⁶				0.72
Proft <i>et al.</i> ⁷⁴				0.83
Davidson <i>et al.</i> ⁸⁰				0.63

The complete active spaces for CH₂ and CH₂⁻ are CAS (6,6) and CAS(7,6), respectively.

Table 7 Electron affinities for $\text{NH}_2(X^2B_1)$ calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP methods

Basis set	Method	$E(\text{NH}_2)/(\text{a.u.})$	$E(\text{NH}_2^-)/(\text{a.u.})$	EA/eV
cc-pVDZ	CASSCF*	-55.614243	-55.529717	-2.300
	CASPT2*	-55.720922	-55.667410	-1.456
	MRPT2*	-55.739575	-55.698871	-1.108
	CCSD	-55.730005	-55.678952	-1.389
	CCSD(T)	-55.732628	-55.682705	-1.358
	B3LYP	-55.877244	-55.841049	-0.985
	X3LYP	-55.850860	-55.812470	-1.045
	M06	-55.836867	-55.803183	-0.917
	HCTH	-55.871626	-55.840280	-0.853
	TPSS	-55.884124	-55.844064	-1.090
	B97D3	-55.842848	-55.806508	-0.989
	mPW2PLYP	-55.818825	-55.776401	-1.154
	B2PLYP	-55.818908	-55.776758	-1.147
cc-pVTZ	CASSCF*	-55.633622	-55.571764	-1.683
	CASPT2*	-55.780268	-55.762187	-0.492
	MRPT2*	-55.799332	-55.798204	-0.031
	CCSD	-55.787983	-55.771587	-0.446
	CCSD(T)	-55.793616	-55.780313	-0.362
	B3LYP	-55.903095	-55.895482	-0.207
	X3LYP	-55.876790	-55.866940	-0.268
	M06	-55.858833	-55.850469	-0.228
	HCTH	-55.895171	-55.889967	-0.142
	TPSS	-55.907703	-55.895617	-0.329
	B97D3	-55.867647	-55.859035	-0.234
	mPW2PLYP	-55.853260	-55.841357	-0.324
	B2PLYP	-55.854298	-55.843271	-0.300
aug-cc-pVDZ	CASSCF*	-55.629003	-55.587679	-1.125
	CASPT2*	-55.738090	-55.753804	0.428
	MRPT2*	-55.749258	-55.789388	1.092
	CCSD	-55.747825	-55.763095	0.416
	CCSD(T)	-55.751737	-55.771696	0.543
	B3LYP	-55.890973	-55.918018	0.736
	X3LYP	-55.864780	-55.889880	0.683
	M06	-55.848869	-55.872388	0.640
	HCTH	-55.885583	-55.919565	0.925
	TPSS	-55.896401	-55.918369	0.598
	B97D3	-55.856069	-55.884304	0.768
	mPW2PLYP	-55.833503	-55.856586	0.628
	B2PLYP	-55.833719	-55.858084	0.663
aug-cc-pVDZ	CASSCF**	-55.633544	-55.607763	-0.702
	CASPT2**	-55.738527	-55.762315	0.647
	MRPT2**	-55.753396	-55.781877	0.775
Exp. ⁸¹				0.77
Curtiss <i>et al.</i> ⁶⁵				0.77
Gill <i>et al.</i> ⁶⁶				0.64
Yeager <i>et al.</i> ⁶⁷				0.53
Ortiz ⁶⁸				0.68
Proft <i>et al.</i> ⁷⁴				0.79
Roos <i>et al.</i> ⁸²				0.73

* The complete active spaces for NH_2 and NH_2^- are CAS(5,6) and CAS(6,6), respectively.

**The complete active spaces for NH_2 and NH_2^- are CAS(7,7) and CAS(8,7), respectively.

4 Conclusions

The electron affinities of F, Cl, OH, SH, CN, CH₂, and NH₂ calculated with CASSCF, CASPT2, MRPT2, CCSD, CCSD(T), B3LYP, X3LYP, M06, HCTH, TPSS, B97D3, mPW2PLYP, and B2PLYP are presented in this study at four levels of basis sets, cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ. MRPT2 results are in very close agreement with the experimental results to within 0.1 eV. Its overall performance is the best among these methods. Density functional theories as a whole are reliable approaches at the aug-cc-pVDZ level though the performance of each individual functional is dependent on the system studied. The performance of CASSCF is inferior to all other methods tested in this study. The wrong sign of the electron affinities of CH₂ and NH₂ calculated with CASSCF even at aug-cc-pVDZ level indicates that CASSCF wavefunction may be not a reliable choice at least for the systems studied here.

It is shown in this work that the diffuse functions play an important role in achieving an accurate result. On the other hand, it is also seen from the results of OH and NH₂ that a relatively large size of the complete active space has a significant effect on the accuracy of the results of MRPT2 since it will introduce higher level of excitation configurations into the zeroth order wavefunction as well as the perturbation wavefunction.

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