A review of computational methods for electron affinity in determined molecules

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A R T I C L E   I N F O

A B S T R A C T

Some density function theories (DFT/ 6 - 311++ G (3 df, 3 pd) basis set   ) methods with as   BPV86, B3PV91, B3LYP, LSDA, MPW1PW91, HCTH,   THCTH, PBE1PBE, PBEPBE, and T PSSTPSS   with Hartree– Fock (HF) and Ab initio methods. These calculations were at quadratic - complete basis set (CBS- Q method). Results of these studies appear that DFT results overestimate and Hartree– Fock results underestimate of EA's values as compared   with experimental calculations. Good convergence with experimental studies of electron affinities in density functional theory methods. Electron affinities of LiBr, NaBr, F_2 and OH diatomic molecules have been calculated using methods above. The electron affinity values that have been extended using THCTH method are overvalued to OH and F2 compounds and dropped to NaBr and LiBr compounds. Also CBS-Q theory or method provides good calculations for OH, LiBr and NaBr molecules, therefore, the electron affinity result is lower than data in experiment one, by (1 eV) that in cases of F2 molecule.

INTRODUCTION

Correct data of Electron Affinity (EA) for different systems are very useful in chemistry field and molecular physics. In the gases discharge, the mixture of electrons attaching gas changes (energy   - electron) distribution and electron density. Recently, some environmental tools to substitute classical electro/attach gas such as SF_6 molecule with gas less greenhouse potential energy makes it important for determine modern systems in this field. Thus, data from laboratories are more difficult to getting for species of many molecular, then the literature for about 100 years of processes of fundamental collisiones of gaseous molecules compounds and slow electrons have been done [1–4]. recently, chemical quantum calculations have become useful to calculate the physical parameters and properties of many quantities such as (EA) of molecules and atoms.

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In accrue case and recently, different density function theories (DFT's) have been used in these studies and the calculations. Therefore, that because the less time overriding and exact results than methods due to method called (ab initio). The various methods of (DFT) give us in general different calculations [5].

NaBr molecule is useful in synthesis of organic compounds as a source to bromide nucleophile to get reactive alkyl bromide from alkyl chloride. Ago , it was important in diatomic system as experimental results for some molecules in diatomic using as a sedative medicament, anticonvulsant and hypnotic. For LiBr molecule, the hygroscopic property leads it important in desiccant in air condition system. F2 molecule is a supremely and more reactive. Therefore , F2 molecule is an special   case because Hrtree Fock results in this molecule appear binding energy in   the negative case.Then the Hydroxyl radical is very reactive. but, OH molecule is useful in chemistry specially in radical chemistry.

In this search we study some states ten out of density functional theory approaches in order to

calculation of(EA) for heteronuclear and homonuclear diatomic moleculs and compare it with (CBS-Q) methods and ab-initio /Hartre – Fock (HF) and experimental results for some molecules in diatomic system as lithium bromide , sodium bromide, fluorine and hydroxyl radical.

Finally, the aim of this work is knowing the computational methods for the electronic affinity of some molecules using different functions

THECOMPUTATIONAL METHODS

In this work, electron affinity have been calculated as difference in zero point vibrational and electronic energy of LiBr , NaBr, F_2, and OH (charged diatomic molecules). The literature works in this calculations have been done by Gaussian program [6]. Then, some different theories and methods to calculate the electron affinity have been focused as following:

1-HF method (6 - 311++ G (3 df, 3 pd) basis set) [7].

2-Hybrid Density Functional Theory methods (6 - 311G++ (3 df, 3 pd) basis sets) which including :

– (LSDA) Local Spin Density Approximation [8]

– (BPV 86) by Perdew's function [9 – 11]

– (B3LYP) function of Lee and Yong - Par by 3 parameter of Beck [9,12]

– (M PW1PW91) which is modified Pedrew - Weng exchange with Perdew / Wang 91 correlation [13 – 18]

– (PBEPBE) which is correlation function of Burke, and Perdew Ernzerh[19,20].

– (PBE1PBE) which is hybrid function of Burke, and Perdew Ernzerh of [19, 20]

–(THCTH and HTCH) functionals of Handy's family with gradient and correlatio– (TPSSTSS) the (generalize gradient approximations) meta-GGA function of Toa- Pedrew-Staroveorv and Scuseria [24]

3- (CBS- Q) higher level for ab initio calculation by complex basis sets quadratic [25,26].ns [21 – 23]

RESULTS AND DISCUSSION

The electron affinities (EA's) for diatomic molecule F2 and OH molecule were compared by many computational methods, for example, by determine kinetic method [27], formation enthalpies of anion relation ship [28], laser photo-detachment method [29] electron appearance energies [30]. So the experimental calculations and results of electron affinity for LiBr molecule don't exist .

By mentioned of value radius and polarizability values [31]. EA of OH molecule studied with LPS (laser - photoelectron spectroscopic) [31] and compared with all data as shown in Table.
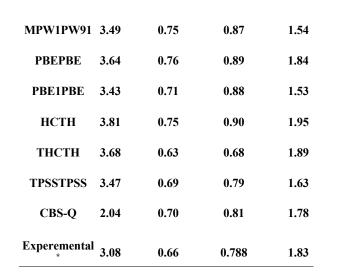
Figure (1) shows the Hartree – Fock and CBS- Q method in F2 molecule undervalues of the electron affinity values as comparing with experimental results and the difference between them is about (-1.04 eV).

However density function theory calculations undervalues electron affinity with good agreement in the midst with the experimental data form (PBE1PBE) function, while there are differences 0.5 eV using MPW1PW91, TPSSTPSS, and B3PV91 functions

As well as, the Differences between experimental and calculated data of EA for LiBr molecule using two methods (DFT/THCTH and HF) undervalue of electron affinity of 0.07 eV for DFT/THCTH and 0.03eV for HF have been obtained as shown in figure 2. Besides, good agreement of computed EA of CBS-Q and TPSSTPSS methods with experimental data of 0.05 and 0,05 ev to be 6% and 5% respectively. On other hand, disagreement of computed EA value of LSDA method of 65% which is 0.43ev have been observed.

Table1. Electron affinity (EA) in eV of LiBr, NaBr, F_2 and OH molecules using different computational methods compared with (experimental) NIST - Database Number (69)[32]

	EA (F_2)	EA (LiBr)	EA (NaBr)	EA (OH)
HF	2.84	0.59	0.71	–0.27
LSDA	3.80	1.09	1.25	2.75
BPV86	3.87	0.81	0.94	1.93
B3LYP	3.72	0.76	0.92	1.75
B3PV91	3.54	0.76	0.88	1.65

MPW1PW91	3.49	0.75	0.87	1.54
PBEPBE	3.64	0.76	0.89	1.84
PBE1PBE	3.43	0.71	0.88	1.53
HCTH	3.81	0.75	0.90	1.95
THCTH	3.68	0.63	0.68	1.89
TPSSTPSS	3.47	0.69	0.79	1.63
CBS-Q	2.04	0.70	0.81	1.78
Experimental *	3.08	0.66	0.788	1.83

Figure. 3 shows the computational results of (EA) for NaBr molecule which have the value more that of LIbr molecule and have convergance calculations perhaps in appears difference in the other physical parameters for these molecules, i.e, dipole moments is 9.6 D for NaBr and 7.1D for LiBr from B3-LYP computational results. In addition for DFT/THCTH and HF calculations the results undervalue of electron affinities about 0.1 and 0.08 eV, respectively. The ideal calculations was of TPSSTPSS functions in density function theory. The (CBS – Q) method give exact results and the deviations in the value of experiment is (0.02 eV), which represent (3%) and disagreement is in (LSDA) method which appear as 60% i.e., 0.46 eV.
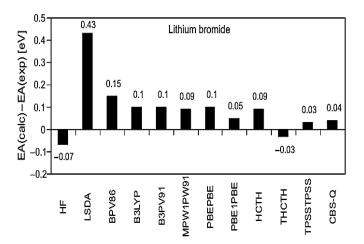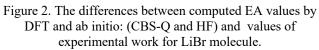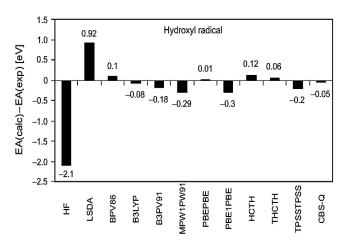

Figure 1. The differences between computed EA values by DFT and ab initio: (CBS-Q and HF) and values of experimental work for F2 molecule.

Figure 3. The differences between experimental and computed results of electron affinity for NaBr molecule.

Figure 2. The differences between computed EA values by DFT and ab initio: (CBS-Q and HF) and values of experimental work for LiBr molecule.
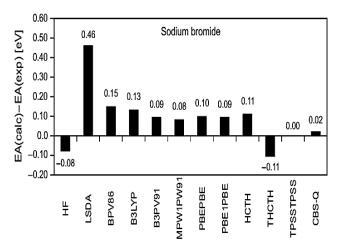

Figure 4. The differences between experimental and computed results of electron affinity for OH molecule.

The calculations for HO molecule have clearly displayed that, B3LYP, B3PV91, HF, PBE1PBE, MPW1PW91, CBS-Q and TPSSTPSS methods undervalue electron affinity value and showed that the highest in the case of the first one which one for the deviation, that mean , more than 110%, 2.1 eV as shown in Figure 4. There are cases of electron molecule affinity is overvalued, furthermost in (LSDA) method, that differences by experimental results is 50% (0.92 eV). The finest agreement with results in experimental data was obtained for B3LYP DFT and THCTH, PBEPBE methods and the (addition CBS-Q) method here agreements with the mentioned results are better than (5%).

For summarize, we can establish that Hartree-Fock theory or method gives mistaken sign of EA for OH molecule. By this theory, the good consistence with experimental data is appear in sodium bromide molecule. The similarity state is for BPV86, HCTH and PBEPBE, by the communication with experimental results is more better. B3PV91, B3LYP, PBE1PBE, TPSSTPSS and MPW1PW91 methods overestimate the data, by the exclusion of OH compound.

The electron affinity values that have been extended using THCTH method are overvalued to OH and F_2 compounds and dropped to NaBr and LiBr compounds. Also CBS-Q theory or method provides good calculations for OH, LiBr and NaBr molecules, therefore, the electron affinity result is lower than data in experiment one, by (1 eV) that in cases of F_2 moelcule.

CONCLUSION

The CBS-Q method appears the best one in methods i.e., The important conclusion From Hartree Fock calculations we can get the negative binding energy specially in F_2 molecule and the electron affinity depending on low unoccupied molecular orbital which is lower than data in experiment one, by (1 eV) specially in F_2 molecule. Therefore, CBS-Q method be the best. The results appear generally that the Hartree- Fock/ 6-311G++(3 df, 3 pd) method undervalues electron affinities, especially in OH. All DFT methods and CBS-Q method gave different calculations and the conclusion from that is due to different bases set in each method.

References

[1] Loucas G. C. & James K. O., Fundamental Electron-Molecule Interactions and Their Technological Significance, Physics of Atoms and Molecules book series (PAMO), Kluwer Academic/Plenum Publishers, New York 2004, pp. 1-59.

[2] James K. O., Electron collision data for plasma-processing gases Advances in Atomic, Molecular, and Optical Physics 44, 2001, 59-98

[3] Karwasz G.Ph., Brusa R.Sh., Zecca A., One century of experiments on electron– atom and molecule scattering. A critical review of integral cross-sections. III. Hydrocarbon and halide, Le Rivista del Nuovo Cimento 24 (4), 2001, pp. 1 – 101.

[4] Karwasz G.P., Zecca A., Brusa R.S., Electron Scattering with Molecules. Total, Landolt– Börstein New Series, Volume I/17, Photon and Electron Interaction, with Atoms, Molecules and Ions, Chapter VI.1., Springer-Verlag, Berlin, Heidelberg, 2003, pp. 6.1 – 6.51.

[5] Dhaidan. K. K , Adil. N. A, Abubaker. S. M., Theoretical Study of Structural Properties and Energies of a 2-Aminophenol -Vanillin Molecule, IOP Conf. Series: Journal of Physics: Conf. Series 1178, 2019, 012007 .

[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M.Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J.A. Montgomery, J.E. Peralta, F. Ogliaro,M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N.Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M.Cossi, N. Rega, J.M. Millam, M. Klene,J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P.Salvador, J.J. Dannenberg, S. Dapprich,. A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowskiand D.J. Fox,l Gaussian 09,Revision, B.01,Gaussian Inc. J. Comput. Chem. 30, 2009, 2785.

[7] Frisch M. Jbinkley J.S., Pople J.A., Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis set, Journal of Chemical Physics 80 (7), 1984, p. 3265.

[8] Lundqvist B.I., Gunnarsson O., Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism, Physical Review B 13 (10), 1976, pp. 4274 – 4298.

[9] Becke A.D., Density-functional thermochemistry. III. The role of exact exchange, Journal of Chemical Physics 98 (7), 1993, pp. 5648 – 5652.

[10] Vosko S.H., Nusair M., Wilk L., Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, Canadian Journal of Physics 58 (8), 1980, pp. 1200 – 1211.

[11] Perdew J.P., Density-functional approximation for the correlation energy of the inhomogeneous electron gas, Physical Review B 33 (12), 1986, pp. 8822 – 8824.

[12] Lee C., Parr R.G., Yang W., Development of the Colle– Salvetti correlation-energy formula into a functional of the electron density, Physical Review B 37 (2), 1988, pp. 785 – 789.

[13] Burke K., Wang Y., Perdew J. P., [In] Electronic Density Functional Theory: Recent Progress and New Directions, [Eds.] Dobson J.F., Vignale G., Das M.P., Plenum, 1998.

[14] Perdew J.P., Electronic Structure of Solids, Akademie Verlag, Berlin, 1991, p. 11.

[15] Perdew J.P., Vosko S.H., Chevary J.A., Jackson K.A., Singh D.J., Pederson M.R., Fiolhais C., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Physical Review B 46 (11), 1992, pp. 6671 – 6687.

[16] Perdew J.P., Vosko S.H., Chevary J.A., Pederson M.R., Jackson K.A., Fiolhais C., Singh D.J., Erratum: Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Physical Review B 48 (7), 1993, p. 4978.

[17] Perdew J.P., Wang Y., Burke K., Generalized gradient approximation for the exchange-correlation hole of a many-electron system, Physical Review B 54 (23), 1996, pp. 16533 – 16539.

[18] Barone V., Adamo C., Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models, Journal of Chemical Physics 108 (2), 1998, pp. 664 – 675.

[19] Perdew J.P., Ernzerhof M., Burke K., Generalized gradient approximation made simple, Physical Review Letters 77 (18), 1996, pp. 3865 – 3868.

[20] Perdew J.P., Burke K., Ernzerhof M., Erratum: Generalized gradient approximation made simple, Physical Review Letters 78 (7), 1997, p. 1396.

[21] Hamprecht F.A., Cohen A.J., Tozer D.J., Handy N.C., Development and assessment of new exchange-correlation functionals, Journal of Chemical Physics 109 (15), 1998, pp. 6264 – 6271.

[22] Boese A.D., Sprik M., Doltsinis N.L., Handy N.C., New generalized gradient approximation functionals, Journal of Chemical Physics 112 (4), 2000, pp. 1670 – 1678.

[23] Boese A.D., Handy N.C., A new parametrization of exchange–correlation generalized gradient approximation functionals, Journal of Chemical Physics 114 (13), 2001, pp. 5497 – 5503.

[24] Tao J.M., Staroverov V.N., Perdew J.P., Scuseria G.E., Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids, Physical Review Letters 91 (14), 2003, p. 146401.

[25] Montgomery J.A., Petersson G.A., Ochterski J.W., A complete basis set model chemistry. IV. An improved atomic pair natural orbital method, Journal of Chemical Physics 101 (7), 1994, pp. 5900 – 5909.

[26] Hout Jr. R.F., Hehre W.J., Levi B.A., Effect of electron correlation on theoretical vibrational frequencies, Journal of Computational Chemistry 3 (2), 1982, pp. 234 – 250.

[27] Artau A., Hill B.T., Nizzi K.E., Wenthold P.G., Sunderlin L.S., Bond dissociation energy in trifluoride ion, Journal of the American Chemical Society 122 (43), 2000, pp. 10667 – 10670.

[28] Squires R.R., Wenthold P.G., Bond dissociation energies of F – and HF –. A gas-phase experimental and G2 theoretical study, The Journal of Physical Chemistry 99 (7), 1995, pp. 2002 – 2005.

[29] Kim J.B., Smith J.R., Lineberger W.C., High-resolution threshold photodetachment spectroscopy

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of OH–, Physical Review A 55 (3), 1997, pp. 2036 – 2043.

[30] Franklin J.L., Harland P.W., Partitioning of excess energy in dissociative resonance capture processes, Journal of Chemical Physics 61 (5), 1974, pp. 1621 – 1636.

[31] Kim J.B., Smith J.R., Lineberger W.C., High-resolution threshold photodetachment spectroscopy of OH–, Physical Review A 55 (3), 1997, pp. 2036 – 2043.

[32] Leopold D.G., Miller T.M., Lineberger W.C., Murray K.K., Electron affinities of the alkali halides and the structure of their negative ions, Journal of Chemical Physics 85 (5), 1986, pp. 2368 – 2375.

[33] NIST Chemistry Web Book, NIST Standard Reference Database Number 69, 2008, National Institute of Standards and Technology, Gaithersburg, MD 20899; http://webbook.nist.gov/chemistry.

مراجعة الطرق الحسابية الى الالفة الالكترونية ولجزيئات محددة

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الخلاصة :

تم استخدام بعض طرق نظريات دالية الكثافة (DFT) مثل BPV86 و B3PV91 و B3LYP و LSDA و MPW1PW91 و HCTH و THCTH و PBE1PBE و PBEPBE و PSSTPSS T مع Hartree– Fock (HF)) وطرق Ab initio لحساب الالفة الالكترونية (EA) لبعض الجزيئات المحددة (جزيئات ثنائية الذرة). كانت هذه الحسابات في طريقة (CBS–Q) (مجموعة أساس تربيعية كاملة). تظهر نتائج هذه الدراسات أن نتائج DFT تبالغ في تقدير نتائج Hartree – Fock تقل من قيم EA مقارنة بالحسابات التجريبية. تقارب جيد مع الدراسات التجريبية للالفة الإلكترونية في طرق نظرية الكثافة الوظيفية. تم حساب الالفة الإلكترونية لجزيئات LiBr و NaBr و F2 و OH ثنائية الذرة باستخدام الطرق المذكورة أعلاه. قيم الالفة الإلكترون التي تم تمديدها باستخدام طريقة THCTH مبالغة في تقديرها لمركبات OH و F2 وتتخفض إلى مركبات NaBr و LiBr. توفر نظرية أو طريقة CBS–Q أيضًا حسابات جيدة لجزيئات OH و LiBr و NaBr ، وبالتالي ، تكون نتيجة الالفة الإلكترون أقل من البيانات الموجودة في التجربة الأولى ، بمقدار (1 eV) في حالة جزيئة F2.

الكلمات المفتاحية: نظرية دالية الكثافة ، الالفة الالكترونية.