

The Evaluation of Molecular Electron Affinities*

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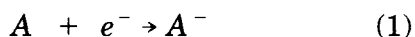
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The performance of a variety of levels of theory in evaluating molecular electron affinities (EAs) has been systematically examined. Calculations have been carried out for six different basis sets and for nine theoretical procedures including unrestricted (UHF) and restricted (RHF) Hartree-Fock theory, Møller-Plesset perturbation theory (UMP2, UMP3, UMP4), configuration interaction (UCISD, RCISD, RCISD(Q)) and equations-of-motion (EOM) approaches. Electron affinities were evaluated for CH₃, NH₂, OH, F, C₂H, CN, BO, N₃, OCN, and NO₂. Very poor results are generally obtained unless diffuse functions are included in the basis set and electron correlation is incorporated. Even with the largest basis set used in the present study (6-311++G(2d, 2p)), there are still residual errors greater than 0.2 eV (UMP4) or 0.6 eV (CISD) in the absolute EAs. However, better results are obtained under certain circumstances for relative EAs. The results appear to be significantly affected by spin contamination in the UHF wavefunctions. For those systems for which spin contamination is small, best absolute values of the EAs generally come from the EOM and UMP2 calculations, whereas the most constant errors (thereby allowing systematic correction) are found at the UMP4, CISD, and RCISD(Q) levels. For the systems for which spin contamination is larger, best results are obtained with the CI-based procedures (CISD and RCISD(Q)). The errors in calculated EAs for the molecules with differing electronic characteristics can vary quite widely. Caution must therefore be exercised before applying schemes which rely on a constancy of errors to estimate electron affinities. The UMP procedures appear particularly suspect in this regard if spin contamination is significant. The RCISD(Q) approach is recommended under such circumstances.

INTRODUCTION

The electron affinity (EA) of a neutral atom or molecule *A* is given by the negative of the energy change in the reaction



A positive EA indicates that the anion is stable while a negative value means that the anion is unstable with respect to electron loss. Typically, EAs are measured in the gas phase by photodetachment, photoelectron or collisional-ionization spectroscopy of the anion *A*[−] [i.e., by the reverse of Eq. (1)].¹ Such electron-detachment energies are normally quite small, indicating that the additional electron in the anion is generally weakly bound.

The accurate theoretical determination of EAs has proved to be difficult.^{2,3} In general, Koopmans' theorem⁴ and the Δ SCF approach (which involves separate Hartree-Fock (HF) calculations on the anion and neutral) yield poor estimates of EAs, leading to the conclu-

sion that incorporation of electron correlation is extremely important for the reliable determination of EAs. This can be readily understood for the case of a closed-shell anion (to which we shall be restricting our attention in this article) by noting that, for this situation, the number of electron pairs in the anion exceeds that in the neutral. The importance of correlation is exemplified by results presented for the hydroxyl radical in the introduction to the 1977 review of negative ions by Simons;² with a reasonably large basis set of Slater functions, the Δ SCF value for the EA is -0.2 eV, whereas when correlation is included an estimate of $+1.76$ eV (compared with the experimental $+1.83$ eV) is obtained.

The fact that there is such a large correlation effect (which is often as large as the entire EA itself), coupled with the difficulty in treating correlation in the ion and the neutral in a balanced manner, has meant that traditional approaches to the calculation of EAs (involving separate calculations on the ion and the neutral) have in general fared poorly. Indeed, systematic studies⁵⁻⁸ of the first-row atoms have suggested that ex-

*Dedicated to Professor John A. Pople on the occasion of his 60th birthday.

tremely large basis sets and high-level incorporation of electron correlation may be needed to obtain EAs that agree consistently with experiment to within 0.1–0.2 eV. For example, using an $[8s5p4d2f1g]$ contracted Gaussian basis set and a multireference configuration interaction procedure, Feller and Davidson⁷ obtained an EA for the oxygen atom that was still in error by 0.17 eV. In another recent systematic study, Raghavachari⁸ found that, in order to obtain EAs for atomic boron, carbon, oxygen, and fluorine to within 0.1 eV of experimental values, a large $[7s6p4d2f]$ basis set and a full fourth-order Møller-Plesset perturbation theory approach were required. However, it would be computationally very expensive to apply such levels of theory to molecules of even moderate size and so it is desirable to explore alternative means of obtaining reliable electron affinities.

One possibility is the equations-of-motion (EOM) or propagator approach.^{9–11} By focusing directly on the quantity of interest (the EA), as in this procedure, there is perhaps a greater prospect of cancellation of errors and hence of obtaining accurate results at modest cost. Indeed, Simons' review article² demonstrates the potential of this technique, reporting reasonably accurate EAs for a number of small molecules using medium-sized basis sets of Slater functions. That the EOM method is capable of predicting ionization energies to within 0.1 eV of experiment is well established.¹²

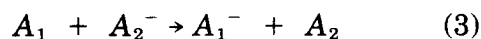
Another approach, which also attempts to avoid the problem of calculating the EA as an energy difference, is to set up a suitable thermodynamic cycle in which suspect or difficult-to-obtain theoretical quantities can be replaced by known experimental values. Thus, Dupuis and Liu,¹³ by replacing the theoretical EA for the carbon atom by the experimental value in the cycle

$$EA(C_2) = D_e(C_2^-) - D_e(C_2) + EA(C) \quad (2)$$

reduced the error in the molecular EA from 0.24 to 0.02 eV. However, as pointed out by Feller and Davidson,⁷ a lack of sufficiently reliable experimental data means that this procedure is not generally applicable.

An even simpler approach is to assume that the errors in EAs, as calculated by energy differences at a given level of theory for related systems, are constant.¹⁴ This is equiv-

alent to assuming that there is only a small error in the calculated energy change for the isogyric¹⁵ reaction



Use of this energy change, coupled with the experimental EA of A_1 for example, allows the electron affinity of A_2 to be estimated. Although this seems an eminently sensible way in which to proceed, we are unaware of it ever having been tested against known experimental data.

In this article, we assess the ability of theory to reproduce the EAs of a small set of molecules for which the experimental values are reasonably well established. Both EOM and conventional approaches, including use of the isogyric reaction [Eq. (3)], are examined. By performing calculations with a range of basis sets and with a variety of theoretical methods, we attempt to assess the levels of theory required to produce reliable electron affinities.

METHOD

Calculations were performed for the ten doublet radicals CH_3 , NH_2 , OH , F , C_2H , CN , BO , N_3 , OCN , and NO_2 and for their closed-shell negative ions. In all cases, geometries optimized at the Hartree-Fock level with the 6-31G(*d*) basis set¹⁶ were employed, with the spin-unrestricted (UHF) formalism being used for the optimizations of the open-shell species. This level of theory has been shown to yield geometries which are, in general, in good agreement with experiment, both for neutrals¹⁷ and anions.^{3b} It is likely that errors in calculated EAs arising from the use of UHF/6-31G(*d*) geometries will generally be small but this should nevertheless be noted as one of the approximations in the present treatment. The optimized geometrical parameters are shown in Table I.

Six basis sets, denoted 6-31G(*d*),¹⁶ 6-31+G(*d*),¹⁸ 6-31++G(*d*, *p*),¹⁸ 6-311++G(*d*, *p*),^{19,20} 6-311++G(2*d*, 2*p*),²⁰ were used in the electron affinity calculations. As an example of this notation, the last basis consists of the standard 6-311G set¹⁹ (in which the valence functions are triply split) augmented on each atom with a set of diffuse functions (denoted ++) and two sets of polarization functions (2*d*, 2*p*).

Table I. Geometries of radicals and anions.^a

Species	Parameter	Anion	Radical
CH ₃	$r(\text{C}-\text{H})$	1.119	1.073
	$\langle \text{HCH} \rangle$	101.7	120.0
NH ₂	$r(\text{N}-\text{H})$	1.030	1.013
	$\langle \text{HNNH} \rangle$	99.3	104.4
OH	$r(\text{O}-\text{H})$	0.962	0.958
CN	$r(\text{C}-\text{N})$	1.161	1.162
BO	$r(\text{B}-\text{O})$	1.227	1.187
C ₂ H	$r(\text{C}-\text{C})$	1.228	1.215
	$r(\text{C}-\text{H})$	1.062	1.058
	$\langle \text{HCC} \rangle$	180.0	180.0
N ₃	$r(\text{N}-\text{N})$	1.156	1.159
	$\langle \text{NNN} \rangle$	180.0	180.0
OCN	$r(\text{C}-\text{N})$	1.167	1.213
	$r(\text{O}-\text{C})$	1.216	1.160
	$\langle \text{OCN} \rangle$	180.0	180.0
NO ₂	$r(\text{N}-\text{O})$	1.229	1.165
	$\langle \text{ONO} \rangle$	116.7	136.1

^aOptimized at the HF/6-31G(d) level. Bond lengths in ångströms, bond angles in degrees. All results from ref. 50 except N₃⁻ (ref. 18a) and BO⁻, N₃, C₂H⁻, and OCN⁻ (present work).

Calculations were carried out with the various basis sets using nine different theoretical procedures. In addition to the EOM approach, calculations were performed with spin-unrestricted (UHF) and spin-restricted (RHF) Hartree-Fock theory, with spin-unrestricted Møller-Plesset perturbation theory²¹ terminated at second (UMP2),²² third (UMP3),²² and fourth (UMP4)²³ orders, and by using a singles-and-doubles configuration interaction (CISD) approach with both UHF (UCISD) and RHF (RCISD) reference configurations for the radicals. Finally, the RCISD results were corrected for the effect of quadruple excitations by using the approximation due to Davidson,²⁴ namely

$$\Delta E_Q \approx (1 - c_o^2)\Delta E_{SD} \quad (4)$$

yielding results referred to as RCISD(Q). In eq. (4), c_o is the coefficient of the RHF configuration in the RCISD wavefunction and ΔE_{SD} is the correlation energy due to single and double excitations. The core molecular orbitals were excluded from all the correlation calculations. The programs used were GAUSSIAN 82,²⁵ ATMOL3,²⁶ and the graphical unitary group (GUGA) CI program of Saxe *et al.*²⁷

The integral and SCF steps for the EOM calculations were performed using the MOLECULE²⁸ and EPSCF²⁹ packages, and the EOM step itself was carried out using a

program written by one of us.³⁰ Details of the method may be found in ref. 11. We used a partial third-order approach (denoted "approximation scheme III" in ref. 11). Such an approach has been found to be successful in the calculation of ionization energies.¹² Apart from the core orbitals (and with the largest basis sets one or two of the highest virtual orbitals), all the molecular orbitals were included in the EOM calculations. The EOM calculations with the 6-311++G(d,p) and larger basis sets employed six second-order Cartesian functions (rather than the standard five pure *d* functions for these sets) but this is unlikely to have affected significantly the resulting EA values.

The results which emerge from the EOM calculations refer to vertical electron detachment from the anion. These values were corrected to give the adiabatic EA by using UMP4 estimates of the difference between the energy of the neutral resulting from such vertical detachment and that of the neutral at its equilibrium structure. In most cases, this correction was negligible; however, for C₂H it amounted to ≈ 0.05 eV and for CH₃, which has a markedly different geometry in the anion compared with the neutral, the correction was 0.7-0.8 eV.

For the smaller systems (CH₃, NH₂, OH, F, CN, and BO), calculations were performed with all of the basis sets and with all nine theoretical procedures. For the larger systems, calculations were carried out only for a subset of this matrix of levels of theory.

RESULTS AND DISCUSSION

The calculated electron affinities for the ten systems examined are displayed and compared with experimental values^{1,31-39} in Tables II-XI, while the deviations of the theoretical values from experiment for four of the basis sets used are given in Tables XII-XV. Species of similar electronic structure are grouped together in these last four tables. We discuss first the conventional methods of obtaining EAs, followed by the EOM approach, and finally comment on the use of isogyric reactions such as (3). We note at this stage that there have been previous *ab initio* estimates⁴⁰⁻⁴⁸ of the electron affinities of most of the species considered here. This previous work is not discussed in detail in the present

Table II. Calculated electron affinities (in eV) for the methyl radical CH_3 .^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(d)	-2.39	-2.51	-1.79	-1.83	-1.77	-1.89	-1.88	-1.82	-1.68
6-31+G(d)	-1.52	-1.63	-0.59	-0.71	-0.57	-0.79	-0.78	-0.66	-0.52
6-31++G(d,p)	-1.50	-1.61	-0.49	-0.61	-0.49	-0.73	-0.72	-0.58	-0.18
6-311++G(d,p)	-1.47	-1.58	-0.34	-0.45	-0.33	-0.60	-0.58	-0.44	-0.01
6-311++G(2d,p)	-1.45	-1.57	-0.21	-0.33	-0.21	-0.50	-0.49	-0.33	0.12
6-311++G(2d,2p)	-1.45	-1.57	-0.19	-0.30	-0.18	-0.49	-0.47	-0.30	
Experiment: 0.08 ± 0.03 (ref. 31)									

^aSee ref. 40 for previous calculations of the electron affinity of CH_3 .**Table III.** Calculated electron affinities (in eV) for the aminyl radical NH_2 .^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(d)	-2.10	-2.22	-1.19	-1.34	-1.29	-1.43	-1.41	-1.35	-1.24
6-31+G(d)	-1.06	-1.18	0.31	-0.01	0.19	-0.11	-0.09	0.05	0.33
6-31++G(d,p)	-1.01	-1.13	0.43	0.10	0.30	-0.02	0.00	0.14	0.47
6-311++G(d,p)	-1.00	-1.12	0.50	0.15	0.39	0.03	0.05	0.20	0.50
6-311++G(2d,p)	-1.01	-1.13	0.60	0.24	0.48	0.10	0.11	0.28	0.64
6-311++G(2d,2p)	-1.00	-1.12	0.66	0.29	0.54	0.14	0.16	0.33	0.68
Experiment: 0.78 ± 0.04 (ref. 32)									

^aSee ref. 41 for previous calculations of the electron affinity of NH_2 .**Table IV.** Calculated electron affinities (in eV) for the hydroxyl radical OH .^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(d)	-1.41	-1.52	-0.21	-0.43	-0.40	-0.52	-0.51	-0.44	-0.25
6-31+G(d)	-0.17	-0.28	1.61	1.12	1.41	1.06	1.07	1.22	1.23
6-31++G(d,p)	-0.15	-0.25	1.68	1.19	1.48	1.11	1.12	1.28	1.95
6-311++G(d,p)	-0.15	-0.25	1.64	1.11	1.49	1.07	1.08	1.24	1.83
6-311++G(2d,p)	-0.15	-0.27	1.77	1.23	1.59	1.15	1.16	1.33	1.92
6-311++G(2d,2p)	-0.15	-0.27	1.82	1.26	1.64	1.18	1.20	1.37	1.98
Experiment: 1.83 ± 0.01 (ref. 1)									

^aSee ref. 42 for previous calculations of the electron affinity of OH .**Table V.** Calculated electron affinities (in eV) for the fluorine atom.^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(d)	-0.31	-0.39	1.07	0.87	0.87	0.79	0.79	0.85	1.05
6-31++G(d,p)	1.37	1.28	3.40	2.91	3.23	2.88	2.88	3.03	3.89
6-311++G(d,p)	1.34	1.25	3.24	2.71	3.08	2.70	2.71	2.85	3.55
6-311++G(2d,2p)	1.34	1.23	3.41	2.86	3.22	2.81	2.82	2.97	3.68
Experiment: 3.40 (ref. 33)									

^aSee ref. 43 for previous calculations of the electron affinity of F .**Table VI.** Calculated electron affinities (in eV) for the ethynyl radical C_2H .^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(d)	1.19	0.70	2.20	2.04	2.09	1.62	1.54	1.53	2.20
6-31+G(d)	1.99	1.52	3.17	2.94	3.06	2.51	2.43	2.46	3.32
6-31++G(d,p)	1.99	1.53	3.20	2.97	3.08	2.53	2.45	2.49	3.58
6-311++G(d,p)	2.02	1.56	3.30	3.07	3.18	2.62	2.54	2.59	3.70
6-311++G(2d,p)	2.01	1.55	3.43	3.20	3.31	2.71	2.63	2.70	
6-311++G(2d,2p)	2.01	1.55	3.44	3.20	3.32	2.71	2.63	2.71	
Experiment: 2.94 ± 0.10 (ref. 34)									

^aSee ref. 44 for previous calculations of the electron affinity of C_2H .

Table VII. Calculated electron affinities (in eV) for the cyano radical CN.^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(<i>d</i>)	2.64	2.20	3.48	3.33	3.26	2.86	2.72	2.59	2.80
6-31++G(<i>d,p</i>)	3.35	2.91	4.42	4.18	4.19	3.70	3.56	3.48	3.77
6-311++G(<i>d,p</i>)	3.37	2.93	4.51	4.26	4.29	3.78	3.64	3.57	4.47
6-311++G(2 <i>d,2p</i>)	3.37	2.93	4.63	4.39	4.42	3.88	3.75	3.70	4.15
Experiment: 3.82 ± 0.02 (ref. 35)									

^aSee ref. 45 for previous calculations of the electron affinity of CN.**Table VIII.** Calculated electron affinities (in eV) for the boroxyl radical BO.^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
6-31G(<i>d</i>)	0.64	0.54	1.12	1.27	1.26	1.11	1.12	1.19	1.33
6-31++G(<i>d,p</i>)	1.49	1.40	2.19	2.27	2.34	2.08	2.10	2.21	2.38
6-311++G(<i>d,p</i>)	1.51	1.41	2.23	2.33	2.40	2.13	2.14	2.27	2.91
6-311++G(2 <i>d,2p</i>)	1.50	1.41	2.32	2.41	2.49	2.19	2.20	2.35	2.97
Experiment: 3.1 ± 0.1 (ref. 36)									

^aSee ref. 46 for previous calculations of the electron affinity of BO.**Table IX.** Calculated electron affinities (in eV) for the azido radical N₃.

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)
6-31G(<i>d</i>)	1.08	0.42	2.46	1.62	2.05	1.39	1.52	1.56
6-31++G(<i>d,p</i>)	1.57	0.91	3.15	2.21	2.74	1.96	2.09	2.16
6-311++G(<i>d,p</i>)	1.56	0.89	3.16	2.17	2.79	1.94	2.08	2.15
Experiment: 2.70 ± 0.12 (ref. 37)								

Table X. Calculated electron affinities (in eV) for the cyanato radical OCN.^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)
6-31G(<i>d</i>)	2.09	1.81	3.05	2.69	2.78	2.50	2.59	2.62
6-31++G(<i>d,p</i>)	2.58	2.30	3.74	3.30	3.46	3.08	3.17	3.23
6-311++G(<i>d,p</i>)	2.57	2.28	3.72	3.26	3.46	3.05	3.15	3.21
Experiment: 3.6 ± 0.2 (ref. 38)								

^aSee ref. 47 for previous calculations of the electron affinity of OCN.**Table XI.** Calculated electron affinities (in eV) for nitrogen dioxide NO₂.^a

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)
6-31G(<i>d</i>)	1.15	0.93	1.08	1.34	1.08	1.19	1.26	1.26
6-31++G(<i>d,p</i>)	1.77	1.56	2.09	2.20	2.11	2.01	2.07	2.15
6-311++G(<i>d,p</i>)	1.73	1.51	1.93	2.05	1.94	1.87	1.94	2.00
Experiment: 2.32 ± 0.04 (ref. 39)								

^aSee ref. 48 for previous calculations of the electron affinity of NO₂.

paper, which is more concerned with generalizations arising from a systematic comparison of results for a variety of molecular systems using standard and widely applicable theoretical procedures.

We should stress two qualifications pertinent to the present analysis. The first is that

the generalizability of our conclusions is limited because of the small number of molecules examined, a restriction imposed by the limited set of suitable small systems for which experimental EAs are available in the literature.¹ The second is that, although for some systems (e. g. OH) the experimental EAs ap-

Table XII. Deviation from experiment of theoretical electron affinities calculated with the 6-31G(d) basis set (in eV).

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
CH ₃	-2.47	-2.59	-1.87	-1.91	-1.85	-1.97	-1.96	-1.90	-1.76
NH ₂	-2.88	-3.00	-1.97	-2.12	-2.07	-2.21	-2.19	-2.13	-2.02
OH	-3.24	-3.35	-2.04	-2.26	-2.23	-2.35	-2.34	-2.27	-2.08
F	-3.71	-3.79	-2.33	-2.53	-2.53	-2.61	-2.61	-2.55	-2.35
C ₂ H	-1.75	-2.24	-0.74	-0.90	-0.85	-1.32	-1.40	-1.41	-0.74
CN	-1.18	-1.62	-0.34	-0.49	-0.56	-0.96	-1.10	-1.23	-1.02
BO	-2.46	-2.56	-1.98	-1.83	-1.84	-1.99	-1.98	-1.91	-1.77
N ₃	-1.62	-2.28	-0.24	-1.08	-0.65	-1.31	-1.18	-1.14	
OCN	-1.51	-1.79	-0.55	-0.91	-0.82	-1.10	-1.01	-0.98	
NO ₂	-1.17	-1.39	-1.24	-0.98	-1.24	-1.13	-1.06	-1.06	

Table XIII. Deviation from experiment of theoretical electron affinities calculated with the 6-31++G(d,p) basis set.

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
CH ₃	-1.58	-1.69	-0.57	-0.69	-0.57	-0.81	-0.80	-0.66	-0.26
NH ₂	-1.79	-1.91	-0.35	-0.68	-0.48	-0.80	-0.78	-0.64	-0.31
OH	-1.98	-2.08	-0.15	-0.64	-0.35	-0.72	-0.71	-0.55	0.12
F	-2.03	-2.12	-0.00	-0.49	-0.17	-0.52	-0.52	-0.37	0.49
C ₂ H	-0.95	-1.41	0.26	0.03	0.14	-0.41	-0.49	-0.45	0.64
CN	-0.47	-0.91	0.60	0.36	0.37	-0.12	-0.26	-0.34	-0.05
BO	-1.61	-1.70	-0.91	-0.83	-0.76	-1.02	-1.00	-0.89	-0.72
N ₃	-1.13	-1.79	-0.45	-0.49	0.04	-0.74	-0.61	-0.54	
OCN	-1.02	-1.30	0.14	-0.30	-0.14	-0.52	-0.43	-0.37	
NO ₂	-0.55	-0.76	-0.23	-0.12	-0.21	-0.31	-0.25	-0.17	

Table XIV. Deviation from experiment of theoretical electron affinities calculated with the 6-311++G(d,p) basis set (in eV).

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
CH ₃	-1.55	-1.66	-0.42	-0.53	-0.41	-0.68	-0.66	-0.52	-0.09
NH ₂	-1.78	-1.90	-0.28	-0.63	-0.39	-0.75	-0.73	-0.58	-0.28
OH	-1.98	-2.08	-0.19	-0.72	-0.34	-0.76	-0.75	-0.59	0.00
F	-2.06	-2.15	-0.16	-0.69	-0.32	-0.70	-0.69	-0.55	0.15
C ₂ H	-0.92	-1.38	0.36	0.13	0.24	-0.32	-0.40	-0.35	0.76
CN	-0.45	-0.89	0.69	0.44	0.47	-0.04	-0.18	-0.25	0.65
BO	-1.59	-1.69	-0.87	-0.77	-0.70	-0.97	-0.96	-0.83	-0.19
N ₃	-1.14	-1.81	0.46	-0.53	0.09	-0.76	-0.62	-0.55	
OCN	-1.03	-1.32	0.12	-0.34	-0.14	-0.55	-0.45	-0.39	
NO ₂	-0.59	-0.81	-0.39	-0.27	-0.38	-0.45	-0.38	-0.32	

Table XV. Deviation from experiment of theoretical electron affinities calculated with the 6-311++G(2d,2p) basis set (in eV).

	RHF	UHF	UMP2	UMP3	UMP4	UCISD	RCISD	RCISD(Q)	EOM
CH ₃	-1.53	-1.65	-0.27	-0.38	-0.26	-0.57	-0.55	-0.38	
NH ₂	-1.78	-1.90	-0.12	-0.49	-0.24	-0.64	-0.62	-0.45	-0.10
OH	-1.98	-2.10	-0.01	-0.57	-0.19	-0.65	-0.63	-0.46	0.15
F	-2.06	-2.17	0.01	-0.54	-0.18	-0.59	-0.58	-0.43	0.28
C ₂ H	-0.93	-1.39	0.50	0.26	0.38	-0.23	-0.31	-0.23	
CN	-0.45	-0.89	0.81	0.57	0.60	0.06	-0.07	-0.12	0.33
BO	-1.60	-1.69	-0.78	-0.69	-0.61	-0.91	-0.90	-0.75	-0.13

pear to be well established, this is not always the case. Consequently discrepancies between theory and experiment for some systems may not be entirely due to errors in the former. Such considerations should be borne in mind in the following sections.

Results of Conventional Molecular Orbital Calculations

Examination of Tables II–XII (particularly Table XII) shows that the results obtained with the smallest basis set [6-31G(*d*)], which lacks diffuse functions, are very poor. Diffuse functions are very important in providing an adequate description of anionic systems¹⁸ and their absence from the 6-31G(*d*) basis set leads to an imbalance in the description of the anion and neutral. The calculated EAs are always too low (Table XII).

The Hartree-Fock results are also generally very poor. The extra electron pair in the anion compared with the neutral means that electron correlation is more important in the anion than in the neutral. Hartree-Fock estimates of electron affinities are therefore normally far too low; as mentioned in the Introduction, inclusion of electron correlation is essential in order to obtain reasonable calculated values.

As in the case of the first-row atoms,⁵⁻⁸ very large basis sets (not attained in the present study) would seem to be necessary to obtain EAs which are consistently within 0.1–0.2 eV of experiment. The fact that the largest basis sets used in the present study give results far from the basis-set limit can be seen, for example, from the large effect of adding a second set of polarization functions to the 6-311++G(*d,p*) basis set, the EA at the UMP4 level typically being increased by ≈ 0.15 eV.

A detailed examination of Tables II–XV indicates that some of the conclusions which may be drawn from the results for CH₃, NH₂, OH, F, and NO₂ are less applicable (to varying extents) to the other systems. These will be discussed individually below. For the moment, we note that the distinction among the set of molecules appears to be associated with the degree of spin contamination in the UHF wavefunctions. For a pure doublet, the expectation value of S^2 would be 0.75. Contamination by states of higher multiplicity

(quartets, sextets, and so on) leads to higher values of $\langle S^2 \rangle$. It can be seen from Table XVI that, whereas the degree of spin contamination is small for CH₃, NH₂, OH, F, and NO₂, there is increasing spin contamination in the UHF wavefunctions for the remaining systems BO, OCN, N₃, CN, and C₂H, with $\langle S^2 \rangle$ values reaching 1.165.

Many of the results of Tables II–XV display a pattern of behavior which is closely linked to the extent of spin contamination. A selection of these results is presented in Table XVI. In the case of the UMP calculations, this pattern may be associated with the recent demonstration by Handy, Knowles, and Somasundram⁴⁹ that the convergence of the Møller-Plesset series can be very slow under certain circumstances, the indication being that this is associated with a heavily contaminated wavefunction. This would lead to an energy for the radical which is too high relative to the closed-shell anion, leading in turn to a calculated EA which may be *greater than* the experimental value. Normally, calculated electron affinities are *less than* experimental values because the (incompletely calculated) correlation energy is greater for the anion than for the neutral. Let us examine these points more specifically.

For the systems with small spin contamination, the UMP2 method yields absolute values of electron affinities in comparable or better agreement with experiment than are values obtained with higher orders UMP3 and UMP4. This appears not to be the case, however, when spin contamination is important (notably for C₂H and CN). The utility of the UMP2 approach for obtaining EAs has been noted previously by Novoa and Mota,^{41b} but we should point out that they did not in-

Table XVI. Expectation values of S^2 for doublet radicals and deviations (in eV) from experiment of theoretical electron affinities (6-311++G(*d,p*) basis set).

Species	$\langle S^2 \rangle$	UMP4	RCISD(Q)
F	0.753	−0.32	−0.55
OH	0.756	−0.34	−0.59
NH ₂	0.758	−0.39	−0.58
CH ₃	0.761	−0.41	−0.52
NO ₂	0.767	−0.38	−0.32
BO	0.797	−0.70	−0.83
OCN	0.835	−0.14	−0.39
N ₃	0.885	0.09	−0.55
CN	1.128	0.47	−0.25
C ₂ H	1.165	0.24	−0.35

investigate systems leading to closed-shell anions for which spin contamination would be a problem.

When spin contamination is small, the UCISD and RCISD results are, as expected, very similar and close to those from UMP3. Even when spin contamination is significant, the UCISD and RCISD results only differ from one another by 0.1–0.2 eV. However, for such systems (e.g. C_2H , CN) there is a substantial difference (≈ 0.5 eV) between the UMP3 and CISD results, perhaps reflecting the slow convergence noted above of the Møller-Plesset expansion under such circumstances.

Examination of the RCISD(Q) results shows that, in all but one case (CN), incorporation of an estimate of the effect of quadruple substitutions brings the RCISD values into closer agreement with experiment.

The difference between the RCISD(Q) and UMP4 results can be attributed largely to the effect of triple excitations, absent from the RCISD(Q) method. Thus, if the contributions to the EA from triple substitutions (as determined from UMP4 calculations) are added to the RCISD(Q) EAs of CH_3 , NH_2 , OH, F, BO, OCN, and NO_2 in Table XVI, the resulting values are in agreement with the UMP4 EAs to within 0.1 eV. As noted previously by Raghavachari,⁸ the triple excitations make a significant contribution (−0.1 to +0.4 eV) to the calculated electron affinities.

For the three systems with the largest degree of spin contamination (N_3 , C_2H , and CN), the poor convergence of the Møller-Plesset expansion also appears to contribute significantly to the difference between the RCISD(Q) and UMP4 results. It is likely, in particular, to be responsible for the *overestimation* of the experimental electron affinities by 0.4 to 0.6 eV at the UMP4/6-311++G(2d,2p) level.

Results of EOM Calculations

Because of program limitations, it was only possible to examine a subset of the total set of molecules with the EOM procedure. The number of comparisons is therefore quite small and the conclusions that are drawn should be regarded as preliminary.

As with the conventional calculations, EOM evaluation of electron affinities with

the 6-31G(d) basis set leads to poor results. This confirms previous conclusions^{43b} that the EOM method does not lead to a noticeably greater cancellation of errors arising from the use of a limited basis set than does a conventional approach. Beyond 6-31G(d), the basis set dependence of the EOM results is similar to that of the conventional calculations.

Absolute values of EOM electron affinities for CH_3 , NH_2 , OH, and F, as calculated with the largest basis sets, are generally in better agreement with experiment than are the values obtained from the UMP and CISD calculations. However, in contrast to the results of the conventional calculations, the errors are far from constant, with the calculated electron affinities lying both higher and lower than the experimental values. Electron affinities calculated by the EOM approach for C_2H and CN are rather poor.

Use of Isogyric Reactions

The aim in using isogyric reactions such as (3) to estimate electron affinities is to exploit the proposition that, whereas absolute values of calculated EAs may have significant errors, these errors are likely to be reasonably constant at a particular level of theory. This would then imply that an accurate value for the energy change in reaction (3) could be obtained and, if the EA for A_1 is known (either from experiment or from very-high-level calculations), the EA for A_2 could be estimated. To what extent is such an approach valid?

Examination of Tables XII–XV shows that, for the isoelectronic series CH_3 , NH_2 , OH, and F, errors in the calculated EAs become more constant as the size of the basis set is increased. Errors also become more constant as the theoretical method is changed from HF to UMP2 to UMP3 to UMP4 and CISD. Thus, with the largest basis set, the errors with the UMP4 method are in the narrow range 0.18–0.26 eV. Errors with the UCISD, RCISD, and RCISD(Q) methods lie in similarly narrow ranges. Clearly, within such a set of closely related systems, the use of the isogyric approach would lead to very accurate estimates of electron affinities.

The situation is less favorable for the second isoelectronic series (C_2H , CN, and BO), for which the errors for a particular theo-

retical method, even with the largest basis set, appear to be quite different from one another and from the errors in the first isoelectronic series. This is particularly noticeable for the Møller-Pesset results which, as we have already noted, may suffer because of the (variable) spin contamination in the UHF wavefunctions for these systems. Use of a UMP4 value for the energy change of the isogyric reaction involving two of these species would lead to a sizeable error in the calculated EA.

If we are seeking a *single* method which may be applied, in conjunction with the isogyric approach, to *all* the systems examined in the present study, the RCISD(Q) approach appears to be the method of choice. A correction of 0.45 eV applied to the RCISD(Q) results with the 6-31++G(*d*,*p*) and 6-311++G(*d*,*p*) basis sets yields EAs for all systems except BO within 0.3 and 0.2 eV, respectively, of the experimental values. The results for BO appear anomalous in this analysis and this could be an indication that the experimentally reported value is somewhat too high.

In general, use of UMP procedures to estimate EAs via the isogyric approach for systems for which the wavefunction is significantly spin-contaminated is not advisable.

CONCLUDING REMARKS

Several important points concerning the evaluation of molecular affinities emerge from the present study.

1. Poor results are generally obtained unless diffuse functions are included in the basis set and electron correlation is incorporated in the theoretical procedure.
2. Even with the largest basis sets used in the present study [6-311++G(2*d*,2*p*)] and with the highest level theoretical procedures (CISD, UMP4) there are significant *absolute* errors in the calculated EAs.
3. Under certain circumstances (see below), good values of *relative* electron affinities may, however, be obtained.
4. Within the limited set of systems to which it has been applied, the EOM approach generally leads to smaller *absolute* errors in EAs than do the conventional molecular orbital methods (the exceptions being

C₂H and CN, where the EOM values are far too high). However, there is less *constancy* or errors with the EOM method.

5. Spin contamination in the UHF-based procedures has an important effect on the calculated electron affinities.
6. For the group of molecules characterized by low UHF spin contamination
 - a. the UMP2 method often yields absolute EAs comparable to or better than values obtained from the other conventional procedures;
 - b. RCISD, UCISD, and UMP3 results are similar to one another; and
 - c. the errors are most constant with the UMP4, UCISD, RCISD, and RCISD(Q) methods, which therefore give rise to good estimates of EAs via the use of isogyric reactions for such systems.
7. For the systems with larger UHF spin contamination
 - a. the most consistent results are obtained with the CISD and RCISD(Q) calculations;
 - b. the RCISD and UCISD results are quite similar, despite the substantial differences between the RHF and UHF starting points;
 - c. the errors are most constant at the RCISD(Q) level. This is therefore the method of choice for the estimation of EAs via the isogyric procedure for systems whose UHF wavefunction is significantly spin-contaminated; and
 - d. it is inadvisable to use UMP procedures to estimate EAs for such systems via the isogyric procedure.

References

1. P.S. Drzaic, J. Marks, and J.I. Brauman, in *Gas Phase Ion Chemistry*, Vol. 3., M. T. Bowers, Ed., Academic, New York, 1984, ch. 21.
2. For a review, see J. Simons, *Ann. Rev. Phys. Chem.*, **28**, 15 (1977).
3. For reviews, see (a) L. Radom, in *Applications of Electronic Structure Theory*, H.F. Schaefer III, Ed., Plenum Press, New York, 1977, ch. 8; (b) R.H. Nobes, D. Poppinger, W.-K. Li, and L. Radom, in *Comprehensive Carbanion Chemistry*, Vol. 3, E. Buncl and T. Durst, Eds., Elsevier, Amsterdam, in press.
4. T. Koopmans, *Physica*, **1**, 104 (1934).
5. F. Sasaki and M. Yoshimine, *Phys. Rev. A*, **17**, 26 (1974).
6. B. Botch and T.H. Dunning, *J. Chem. Phys.*, **76**, 6046 (1982).

7. D. Feller and E. R. Davidson, *J. Chem. Phys.*, **82**, 4135 (1985).
8. K. Raghavachari, *J. Chem. Phys.*, **82**, 4142 (1985).
9. T. T. Chen, W. D. Smith, and J. Simons, *Chem. Phys. Lett.*, **26**, 296 (1974).
10. W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *J. Chem. Phys.*, **67**, 4124 (1977).
11. J. Baker, *Chem. Phys.*, **79**, 117 (1983).
12. See, for example, J. Baker and B. T. Pickup, *Mol. Phys.*, **49**, 651 (1983).
13. M. Dupuis and B. Liu, *J. Chem. Phys.*, **73**, 337 (1980).
14. See, for example, G. Winkelhofer, R. Janoschek, F. Fratev, G. W. Spitznagel, J. Chandrasekhar, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **107**, 332 (1985).
15. J. A. Pople, M. J. Frisch, B. T. Luke, and J. S. Binkley, *Int. J. Quantum Chem. Symp.*, **17**, 307 (1983).
16. (a) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973); (b) J. S. Binkley and J. A. Pople, *J. Chem. Phys.*, **66**, 879 (1977).
17. D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **101**, 4085 (1979).
18. (a) T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comput. Chem.*, **4**, 294 (1983). (b) G. W. Spitznagel, T. Clark, J. Chandrasekhar, and P. v. R. Schleyer, *Ibid.*, **3**, 363 (1982). (c) J. Chandrasekhar, J. G. Andrade, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5609 (1981).
19. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).
20. M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.*, **80**, 3265 (1984).
21. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
22. J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, **10**, 1 (1976).
23. (a) R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.*, **14**, 91 (1978); (b) R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.*, **72**, 4244 (1980).
24. E. R. Davidson, in *The World of Quantum Chemistry*, R. Daudel, Ed., Reidel, Dordrecht, 1974, pp. 17-30.
25. J. S. Binkley, M. J. Frisch, D. J. Defrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, *Gaussian 82*, Carnegie-Mellon University, Pittsburgh, PA 15213, USA.
26. M. F. Guest and V. R. Saunders, *ATMOL3 User Manuals*, Rutherford Laboratory, Science Research Council (UK), 1976.
27. P. Saxe, D. J. Fox, H. F. Schaefer III, and N. C. Handy, *J. Chem. Phys.*, **77**, 5584 (1982). We thank Drs. N. C. Handy and R. J. Harrison for supplying us with a copy of this program.
28. J. Almlöf, *Report 74-29*, Institute of Physics, University of Stockholm, Stockholm, Sweden.
29. N. H. Beebe, G. D. Purvis, and H. A. Kurtz, Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA.
30. J. Baker, *EOM*, Department of Quantum Chemistry, University of Uppsala, Uppsala, Sweden.
31. G. B. Ellison, P. C. Engelking, and W. C. Lineberger, *J. Am. Chem. Soc.*, **100**, 2556 (1978).
32. R. J. Celotta, R. A. Bennett, and J. L. Hall, *J. Chem. Phys.*, **60**, 1740 (1974).
33. (a) H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **4**, 539 (1975); (b) H. Hotop and W. C. Lineberger, *Ibid.*, **14**, 731 (1985).
34. B. K. Janousek, J. I. Brauman, and J. Simons, *J. Chem. Phys.*, **71**, 2057 (1979).
35. J. Berkowitz, W. A. Chupka, and T. A. Walker, *J. Chem. Phys.*, **50**, 1497 (1969).
36. R. D. Srivastava, O. M. Uy, and M. Farber, *Trans. Faraday Soc.*, **67**, 2941 (1971).
37. R. L. Jackson, M. J. Pellerite, and J. I. Brauman, *J. Am. Chem. Soc.*, **103**, 1802 (1981).
38. C. A. Wight and J. L. Beauchamp, *J. Phys. Chem.*, **84**, 2503 (1980).
39. (a) S. B. Woo, E. M. Helmy, P. H. Mauk, and A. P. Paszek, *Phys. Rev. A*, **24**, 1380 (1981); (b) E. Herbst, T. A. Patterson, and W. C. Lineberger, *J. Chem. Phys.*, **61**, 1300 (1974).
40. CH₃: (a) F. Driessler, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, *Theor. Chim. Acta*, **30**, 315 (1973); (b) G. T. Surratt and W. A. Goddard III, *Chem. Phys.*, **23**, 39 (1977); (c) D. S. Marynick and D. A. Dixon, *Proc. Natl. Acad. Sci. USA*, **74**, 410 (1977); (d) H. Kollmar, *J. Am. Chem. Soc.*, **100**, 2665 (1978).
41. NH₂: (a) J. V. Ortiz and Y. Öhrn, *Chem. Phys. Lett.*, **7**, 548 (1981). See also ref. 2. (b) J. J. Novoa and F. Mota, *Chem. Phys. Lett.*, **123**, 399 (1986).
42. OH: (a) J. J. Novoa and F. Mota, *Chem. Phys. Lett.*, **119**, 135 (1985); (b) D. M. Chipman, *J. Chem. Phys.*, **84**, 1677 (1986) and references therein. We thank Dr. Chipman for a preprint of this paper. See also ref. 41b.
43. F: (a) L. S. Cederbaum, K. Schönhammer, and W. von Niessen, *Phys. Rev. A*, **15**, 833 (1977); (b) M. F. Herman, K. F. Freed, D. L. Yeager, and B. Liu, *J. Chem. Phys.*, **72**, 611 (1980). See also refs. 5, 6, and 8 and references therein.
44. C₂H: (a) J. E. Williams, Jr. and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975); (b) J. Pacansky and G. Orr, *J. Chem. Phys.*, **67**, 5952 (1977); (c) K. Vasudevan and F. Grein, *J. Chem. Phys.*, **68**, 1418 (1978); (d) W.-K. Li, R. H. Nobes, and L. Radom, *J. Mol. Struct., Theochem*, in press. See also ref. 34.
45. CN: (a) K. M. Griffing and J. Simons, *J. Chem. Phys.*, **64**, 3610 (1976); (b) B. Liu, *J. Chem. Phys.*, **67**, 373 (1977); (c) J. Pacansky and B. Liu, *J. Chem. Phys.*, **66**, 4818 (1977); (d) P. R. Taylor, G. B. Bacskay, N. S. Hush, and A. C. Hurley, *J. Chem. Phys.*, **70**, 4481 (1979); (e) J. V. Ortiz, R. Basu, and Y. Öhrn, *Chem. Phys. Lett.*, **103**, 29 (1983); (f) L. L. Lohr, *J. Phys. Chem.*, **89**, 3465 (1985).
46. BO: A. Heiberg, J. Almlöf, and A. V. Nemukhin, *Chem. Phys. Lett.*, **88**, 399 (1982). See also ref. 2.
47. OCN: W.-K. Li, J. Baker, and L. Radom, *Aust. J. Chem.*, in press.
48. NO₂: E. Andersen and J. Simons, *J. Chem. Phys.*, **66**, 2427 (1977). See also ref. 2.
49. N. C. Handy, P. J. Knowles, and K. Somasundram, *Theor. Chim. Acta*, **68**, 87 (1985).
50. R. A. Whiteside, M. J. Frisch, and J. A. Pople, Eds., *Carnegie-Mellon University Quantum Chemistry Archive*, Third Ed. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213, USA, 1983.