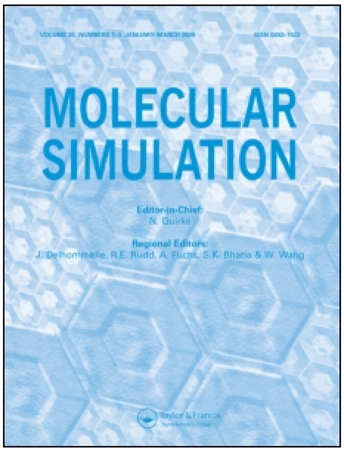

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THE CALCULATION OF THE ELECTRON AFFINITY OF ATOMS AND MOLECULES

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Non-local density functional theory, as implemented in the code DMol, has been used to calculate the electron affinity of a set of 44 small atoms and molecules. A judicious choice of basis sets produces a root mean square deviation from recommended values of 0.1 eV and 0.3 eV for atoms and small molecules (with positive electron affinities) respectively. Applying DMol to calculations of temporary anion states or resonances of linear alkanes to $n = 36$ (where n is the number of carbon atoms) a gradual increase in electron affinity is predicted which appears to have converged by $n = 36$ to -0.75 eV (in agreement with experimental data for C_{36} and polyethylene).

Keywords: Electron affinity; DMol; alkanes; metastable states

1. INTRODUCTION

The electron affinity, representing one half of an electron transfer process (with the ionisation potential) plays a central role in gas and condensed phase chemistry. Data on electron affinities are important [*e.g.*, 1, 2] in theories of chemical reaction and intermediate species, for biochemistry (biological redox processes, radiation damage), to our understanding of chemical bonds and in theories of electronic devices (semiconductors, dielectrics).

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An *adiabatic* electron affinity can be defined as

$$EA_a = E(R_e) - E^-(R_e^-) \tag{1}$$

where $E(R_e)$ is the total (ground state) energy of the neutral species in its equilibrium geometry R_e and $E^-(R_e^-)$ is the total energy of the anion in its minimum energy geometry. If the anion is not allowed to relax on electron attachment, a *vertical* electron affinity is defined through

$$EA_v = E(R_e) - E^-(R_e) \tag{2}$$

the total energies being calculated in the equilibrium geometry of the neutral species.

The total energy of a molecule can be resolved into an electronic (E_{el}) and nuclear contribution, taken to be the vibrational ground state of the nuclear motion, the zero point energy (ZPE). The adiabatic electron affinity then becomes (*e.g.* [3])

$$EA_a = E_{el}(R_e) - E_{el}^-(R_e^-) + ZPE - ZPE^- \tag{3}$$

The vertical affinity contains only the electronic energy

$$EA_v = E_{el}(R_e) - E_{el}^-(R_e) \tag{4}$$

There are a large number of experimental techniques, which have been applied to the determination of electron affinities including laser photoelectron spectroscopy [4], electron transmission spectroscopy [5], and gas phase ion-molecule equilibria [6]. A description of thirty-one methods for the determination of electron affinities may be found in reference seven. Despite the number of techniques available, the reliable determination of electron affinities still represents a considerable challenge, especially for large molecules where it may be difficult to use accurate gas phase techniques. There is a particular difficulty where the electron affinity is negative and the anion is consequently short lived (see [5] for a full discussion of the experimental techniques used to obtain electron affinities for temporary anions). This is the case for the alkanes discussed in the second part of the present article where (with the exception of methane) gas phase methods such as electron transmission spectroscopy cannot resolve the resonant states. There is a need for fast and reliable theoretical methods of calculating electron affinities. Data are available [43] for hexatriacontane (C_{36}) from photoemission spectroscopy of C_{36} monolayers on Cu(111) as well as for polyethylene [44].

Ab initio methods of calculating electron affinities have been reviewed (to 1987) by Simons and Jordan [8] who point out the need for flexible basis sets and a careful treatment of electron correlation effects in order to obtain accurate electron affinities. They state that 'it is extremely difficult to reliably calculate electron affinities within an accuracy of better than 0.2 eV for most classes of atoms and molecules' and call for the development of new theoretical and computational tools.

More recent *ab initio* work [9] using multireference singles and doubles configuration interaction (MRSD-CI) with specialised correlation-optimised and augmented basis sets applied to H, B, C, O and F obtained a root mean square deviation from recommended experimental values of the electron affinities of 0.05 eV, demonstrating that it is possible to achieve high accuracy for small atoms, albeit at considerable computational expense (see also [10]). A detailed study of specialised exchange correlation functionals within density functional theory [11] reports average deviations of around 0.2–0.4 eV for atoms with atomic number less than or equal to 20.

Due to the complexity of the calculations, electron affinities for molecules are usually reported for individual species or small groups of related species. For example, electron propagator methods give excellent results [12] for the electron affinity of C_4^- (3.69 eV compared to experimental results of 3.7 and 3.88 eV). For BO_2 the electron affinity is within 0.4 eV of the experimental data [13]. The use of semiempirical CNDO type calculations to explore unoccupied σ^* orbitals and hence estimate electron affinities for a number of small hydrocarbon and fluorocarbon molecules has been reported [14]. Reasonable agreement was obtained between calculated and experimental energies (see Tab. III below). There have been few assessments of the accuracy of DFT calculations of electron affinity for molecules. In a 1992 paper, Ziegler and Gutsev [15] reported non-local density functional theory (NLDFT, see Section 2 below) calculations for 11 small molecules and found a rms deviation of ~ 0.3 eV (recalculated from Tabs. II and V of Ref. [15]).

Although there has been a significant amount of work on both the measurement and the calculation of electron affinities for atoms, molecules, clusters and solids we are far from having sufficient reliable data. The present work constitutes an exploration of the use of density functional theory (as expressed in the widely available code DMol) to calculate electron affinities for a representative sample of small atoms and molecules having both positive and negative values of the electron affinity. We wish to assess the accuracy of a routine DMol calculation of electron affinity *i.e.*, a calculation that has not been tailored to a particular species. In addition, we are particularly interested in the electron affinity of alkanes and its variation with molecular conformation: a subject little explored to date. Data on alkane electron affinities is central to new approaches to space charge and dielectric breakdown in polyethylene [47].

In the following section, we briefly review density functional theory and the code DMol. In section three we present the results of applying DMol to some 44 small atoms and molecules and make a comparison with recommended experimental results. Section four considers the alkanes and reports electron affinities for straight chain alkanes up to carbon number 36.

2. DENSITY FUNCTIONAL THEORY AND DMOL

The calculations reported in this work have been carried out using non-local density functional theory (NLDFT) as implemented in the DMol code [16]. For comparison, some calculations have been done with Hartree-Fock theory using Gaussian94 [49]. Density functional theory has been described in detail elsewhere [17] and only a very brief description is given below.

DFT starts with a theorem by Hohenberg and Kohn [18] that all ground state properties are functions of the electron density ρ. As a result, the total energy may be written as:

$$E_T[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \tag{5}$$

Where $T[\rho]$ is the kinetic energy of a system of non-interacting particles of density ρ, $U[\rho]$ is the electrostatic interaction due to Coulomb interactions between electrons and nuclei, and $E_{xc}[\rho]$ includes all many body contributions to the total energy (exchange and correlation energies). The wavefunction ϕ is an antisymmetrised product of one-electron functions representing molecular orbitals such that the electron density is given by the sum over all occupied molecular orbitals.

$$\rho(r) = \sum |\phi_i(r)|^2 \tag{6}$$

The energy terms can then be written exactly in terms of ϕ and ρ, however the exchange-correlation term requires approximation to be tractable. The *local* density approximation assumes that the electron density varies slowly and can be represented locally by a uniform electron gas (having energy $\varepsilon_{xc}[\rho]$ at density ρ) so that

$$E_{xc}[\rho] = \int \rho(r)\varepsilon_{xc}[\rho]dr \tag{7}$$

The inhomogeneity of the electron gas can be represented by a gradient expansion (*non local* DFT) giving a gradient 'd' corrected exchange-correlation energy $E_{xc}[\rho, d(\rho)]$.

Varying the total energy with respect to each wavefunction ϕ_i yields the Kohn-Sham equations

$$(T + V(r) + \mu_{xc})\phi_i = \varepsilon_i\phi_i \tag{8}$$

where μ_{xc}, the exchange-correlation potential arises from the differentiation of E_{xc}. It is common practice to expand the molecular orbitals in terms of atomic orbitals

$$\phi_i = \sum C_{i\mu}\chi_\mu \tag{9}$$

where the χ_μ constitute the atomic basis functions. In the DMol implementation, the atomic basis functions are given numerically as values on an atomic centred spherical polar mesh. The code DMol solves the KS equations to find the electron density distribution corresponding to the lowest ground state energy.

In DMol the basis set comprises occupied atomic orbitals for the neutral atoms and for the +2 atomic cations, except for hydrogen where a nuclear charge of +1.3 is used. This basis set is referred to as Double Numeric (DN). Adding a function on each atom with one angular momentum unit higher than that of its highest occupied orbital (*i.e.*, p for H, d for C) leads to a double numerical with polarization function (DNP) basis set. This basis set is referred as DMol 1 in the tables. Additional functions beyond the DNP basis set are available. A hydrogenic calculation with a nuclear charge of $+\zeta$ (variable for each system studied, see Tabs. I and II) provide additional s p and d orbitals. This basis set (DNP+) is referred to as DMol 2 in Tables I and II. To illustrate the use of diffuse functions, the hydrogenic function (1s) is given below:

$$\left(\frac{3}{4\Pi}\right)^{1/2} \cos\Theta \times 2\left(\frac{\zeta}{a_0}\right)^{3/2} \exp\left(-\frac{1}{2}\left(\frac{2\zeta r}{a_0}\right)\right) \tag{10}$$

By varying ζ the spatial extent of the orbital can be increased. This leads to diffuse functions when ζ is small compared to Z, the atomic number (*e.g.*, less than 1 for H, or less than 6 for C). As functions are added to the basis set, they are orthogonalised with respect to those already in the set and are not included if linearly dependent. With Gaussian94 the basis sets were

TABLE I Electron affinity of atoms H to Ar, comparison with experiment

Elements	*EA**	*DMol* 1	*error*	*DMol* 2	*error*	ζ *parameter***
Positive electron affinities						
H	0.75	−0.096	−0.846	0.741	−0.08	0.3***
Li	0.62	0.24	−0.38	0.42	−0.2	0.02
B	0.24	0.22	−0.02	0.25	0.01	3
C	1.27	1.31	0.04	–	–	–
O	1.46	1.21	−0.34	1.39	−0.07	3
F	3.34	3.26	−0.08	3.42	0.08	4
Na	0.55	0.17	−0.38	0.41	−0.14	0.02
Al	0.46	0.4	−0.06	0.41	−0.05	4
Si	1.38	1.4	0.02	1.41	0.03	2
P	0.74	0.47	−0.27	0.68	−0.06	1
S	2.08	2	−0.08	2	−0.08	2
Cl	3.61	3.54	−0.07	–	–	–
RMSD			0.32		0.1	
Negative electron affinities						
He	−0.22****	−10.78	−10.56	−0.28	−0.06	0.02***
Be	−0.19	−2.21	−2.02	−0.21	−0.02	0.02
N	−0.07	−0.75	−0.68	−0.08	−0.01	1.2
Ne	−0.3****	−28.02	−27.72	−0.38	−0.08	0.02
Mg	−0.22	−5.44	−5.22	−0.18	0.04	0.02
Ar	−0.36****	−12.86	−12.5	−0.38	−0.02	0.02
RMSD			13.3		0.05	

Note: Electron affinities in eV,
* literature values taken from J. Emsley, The Elements, second edition, Oxford University Press 1992,
** adjustable diffuse function orbital exponent,
*** only *s* and *p* diffuse functions added,
**** (calculated). DMol 1, VWN, B88, PW, DNP, fine mesh, DMol 2, VWN, B88, PW, DNP++, fine mesh.

6-31G^{**}, 6-31++G^{**} and 6-311++G^{**} [50]. Where appropriate post Hartree-Fock treatments have also been employed.

3. ELECTRON AFFINITIES OF ATOMS AND SMALL MOLECULES

3.1. Atoms

Table I reports the electron affinities of atoms *H* to Ar obtained using DMol separated into two groups having positive and negative electron affinities (*EA*). For the first group DMol predicts the electron affinity to a root mean square deviation of 0.3 eV (0.2 eV if *H* is excluded), if diffuse functions are added the rms. deviation is reduced to 0.1 eV. These results compare well with those reported for *ab initio* methods (MP2, MP4, CIPSI [10], and MRSD-CI [9]) and for specialised exchange correlation functionals within DFT treatments [11] for first row atoms. For the second group of atoms

TABLE II Adiabatic electron affinity of small molecules: Comparison with experiment

Molecule	*Rec. val.*	*Reference*	*DMol 1 + ZPE*	*Error*	*DMol 2 + ZPE*	*Error*	*ΔZPE*
			Positive electron affinity				
NO	0.033 ± 0.01	25	0.218	0.185	0.257	0.224	0.063
CH3	0.08 ± 0.03	26	0.142	0.062	0.16	0.08	0.062
P2	0.23 ± 0.23	27	0.576	0.346		0.346	0.016
O2	0.451 ± 0.007	28	0.264	−0.187	0.504	0.053	0.054
NH2	0.744 ± 0.022	29	0.879	0.135		0.135	0.099
SO2	1.097	27	1.356	0.259		0.259	0.056
PH2	1.25 ± 0.03	29	1.158	−0.092	1.242	−0.008	0.028
OH	1.8276	30	2.045	0.217		0.217	−0.025
SH	2.319 ± 0.01	31	2.302	−0.017	2.333	0.014	0.002
CL2	2.38 ± 0.1	32	2.782	0.402		0.402	0.042
BF3	2.65	32	−0.556	−3.206	2.744	0.094	0.134
N3	2.76 ± 0.004	33	2.704	−0.056	2.736	−0.024	−0.046
F2	3.08 ± 0.1	32	3.569	0.489		0.489	0.089
NO2	2.11 ± 0.2	34	1.88	−0.23	2.13	0.02	0.06
HCO2	3.498 ± 0.015	35	3.161	−0.337	3.261	−0.237	0.021
PO3	3.5	36	4.349	0.849		0.849	−0.071
C2	3.54	27	2.56	−0.98	3.45	−0.09	−0.02
OCN	3.6 ± 0.2	13	3.43	−0.17		−0.17	−0.04
BO2	4.25	37	4.02	−0.23		−0.23	−0.06
NO3	3.77 ± 0.25	36	3.325	−0.445	3.405	−0.365	−0.065
CN	3.821 ± 0.004	38	3.547	−0.274	3.797	−0.024	0.007
RMSD:				0.79		0.28	
			Negative electron affinity				
N2	−1.9 ± 0.1	39	−1.953	0.053		0.053	0.067
C2H4	−1.768	7	−1.68	−0.088		−0.088	–
H2	−0.78	7	−1.82	1.04	−1.04	0.26	0.14
CO	−1.8 ± 0.1	40	−1.715	−0.085		−0.085	0.065
CO2	−0.6 ± 0.2	41	−0.712	0.112		0.112	0.088
RMSD:				0.47		0.14 0.09*	

Note: All values in electron volts. DMol 1, VWN, B88, PW, DNP. DMol 2, VWN, B88, PW, DNP++, *excluding hydrogen.

having negative electron affinities DMol gives large errors that can be reduced almost to zero using diffuse functions. Diffuse functions have a well-known role in obtaining realistic energies of small anions [22]. For molecules that have a positive affinity, the diffuse functions expand the basis set so that the anion can find its equilibrium geometry. For a molecule with a negative affinity, the diffuse functions monotonically lower the energy of the anion to that of the neutral. This result represents the computational equivalent of electron autodetachment, and as a result, the properties of these anionic states in vacuum appear to be mathematically indeterminate in variational *ab-initio* treatments [23]. However, it is possible to artificially stabilise such anion states by varying parameters in the Hamiltonian [24] or through a judicious choice of functional and/or basis set such that *ab-initio* calculations of negative electron affinities yield values consistent with experimental data. In the condensed phase, temporary anionic states may be stabilised by the environment (see for example the work of Ewig on ionic crystals [23], also [52]).

3.2. Molecules

Ziegler and Gutsev [15] reported NLDFT calculations for 11 small molecules and found a rms. deviation of ~0.3 eV. For the larger group studied here the same rms deviation is obtained (Tab. II, Fig. 1). However, Jursic

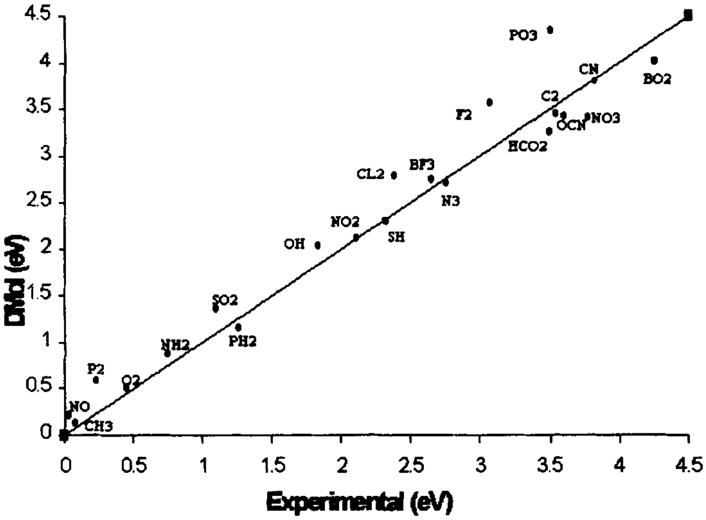

FIGURE 1 Positive electron affinity.

[48] has obtained deviations of about 0.05 eV for three small radicals using DFT. For molecules with negative electron affinities the rms deviation is 0.5 eV including H_2, and 0.1 eV excluding hydrogen (Tab. II, Fig. 2). At least for this group of molecules DMol without diffuse functions appears to produce accurate estimates of negative molecular electron affinities. In Section 4 we use DMol to study the (negative) electron affinities of alkanes.

3.3. Metastable Anions

Metastable anions can be divided into two general types: shape resonance and core-excited resonance (Fig. 3). In the former case the extra electron is attached to the molecule *via* a permanent and induced dipole moment

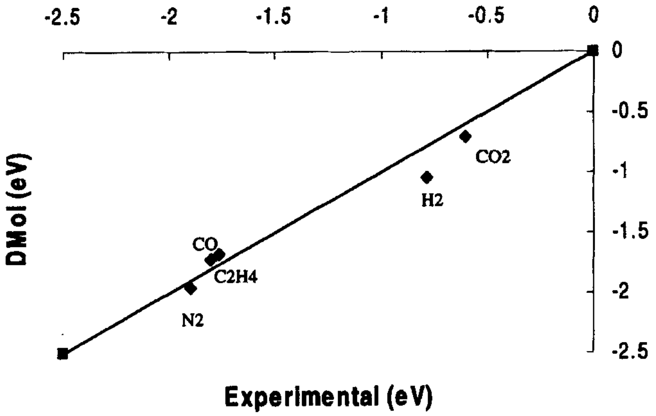

FIGURE 2 Negative electron affinities.

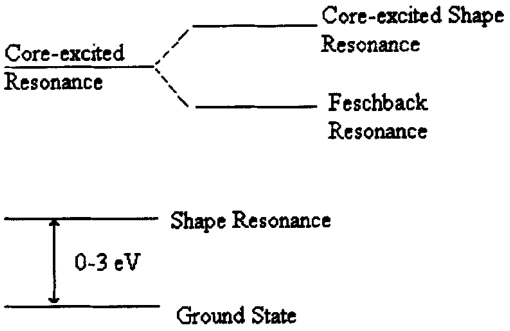

FIGURE 3 Resonances.

(examples are ^{2}P anion state of Mg, π^* states of N2, CO). This occurs when an incident electron with non-zero angular momentum is temporarily captured in the ground state of a molecule [55, 56]. In the later case the electron is attached to an excited state of the neutral molecule [8]. These core-excited resonances (also referred as two-particle one-hole, [5]) can also be divided in two groups: Feschback resonances, wherein their energy lies below the excited neutral parent, and core-excited shape resonances, wherein their energy lies above their neutral excited parent.

In order to elucidate the behaviour of the total energy from DMol for metastable anions, the variation of anionic energy with respect to diffuse functions has been investigated. The energy of both the neutral and the anion were computed for various basis sets following the addition of diffuse functions. In our calculations the energy of the neutral atom or molecule was essentially independent of the addition of extra diffuse functions as expected. The CN example is given below ($EA + 3.821$ eV) in Figure 5. In contrast for molecules having negative electron affinities, the SCF energy of the anions with the addition of diffuse functions changes considerably. In all cases the addition of diffuse functions stabilises the anion; only slight variations were observed on addition of further diffuse functions until a point where the SCF energy suddenly drops and tends toward that of the neutral species. At this point there are sufficient diffuse functions to allow the electron to separate from the molecule. A typical result is given below for the tridecane molecule (Fig. 4):

From Figures 4 and 5 we see that where the electron affinity is too negative (metastable anion) adding diffuse functions can reduce the error (at

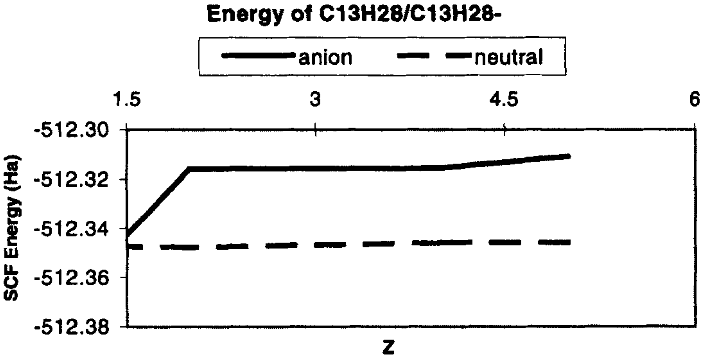

FIGURE 4 SCF energy variation of a tridecane molecule (see Section 6) with respect to added diffuse functions. Z represents the diffuse character of the basis set, the smaller Z the more diffuse the added functions in the basis set.

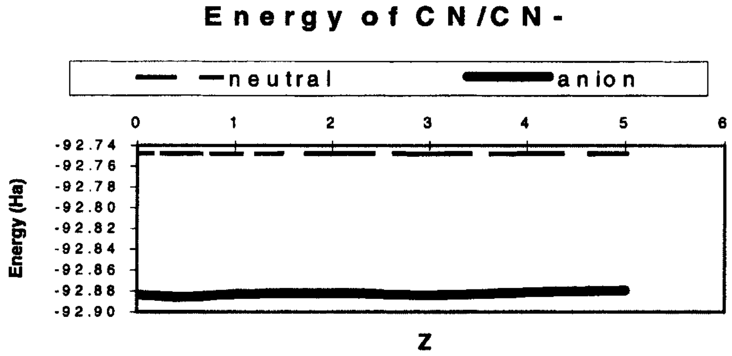

FIGURE 5 SCF energy variation of the neutral and anionic CN molecule, with respect to the diffuse functions added.

the cost of moving away from the plateau value, see Fig. 4). If the electron affinity is negative but too large then the addition of diffuse functions will not improve the result. For the case of positive electron affinities where DMol 1 provides a good estimate of the electron affinity, addition of diffuse functions does not significantly change the results (Fig. 5 and Tabs. I and II).

These calculations demonstrate that, for some molecules, DMol predicts metastable states (*cf.* plateau in Fig. 4) with respect to the electron and neutral molecule at infinity. The values of these metastable states are consistent with measured negative electron affinities. In what follows DMol without diffuse functions (DMol 1) is used to investigate the negative anions of alkanes.

4. ELECTRON AFFINITIES OF ALKANES

Very few experimental data for the electron affinity of linear alkanes can be found in the literature. Data exists for methane [42], Hexatriacontane [43] and polyethylene [44]. The value of $-5\,\text{eV}$ for methane suggests that small alkane anions are metastable and difficult to observe [see for example [45]). Intermediate anion states of alkanes dissociate mainly *via* H^- elimination:

$$C_nH_{2n+2} + e- \rightarrow (C_nH_{2n+2})^- \rightarrow C_nH_{2n+1} + H^-$$

According to P. Rowentry *et al.* [53] these transient anions are core-excited resonance states. Jordan and Burrow reporting [5] unpublished work on methane and others alkanes state that "the extra electron must go into a "Rydberg type" orbital". They also report the absence of evidence of low-lying shape resonances due to capture by σ^* orbitals. The extra electron goes in an orbital of high energy, of the Rydberg type. Hence, this orbital is much higher in energy than the LUMO. Within Koopman's theorem, the *EA* of a molecule (atom) is related to the energy of the energy of the LUMO $\varepsilon_{\mathrm{LUMO}}$ by:

$$EA = -\varepsilon_{\mathrm{LUMO}} \tag{11}$$

Koopmans' theorem could not be applied in the present case for two reasons (1) the *EA* can be linked to minus the energy of an orbital, but this orbital has to be the one accepting the extra electron, which in that case is not the LUMO and (2) Koopmans' theorem refers to single determinant Hartree-Fock, not DFT, wave functions.

In order to obtain electron affinities the excited states should be computed. Then, the extra electron can be added in an orbital of Rydberg type. This procedure could not be followed with the software used in this study. Instead, the extra electron has been added to the LUMO of the neutral ground state of the molecule. Fortunately, there is a cancellation of errors in the procedure used here. The anion is too stable because its parent is in the ground state, but the correlation energy, due to the extra electron, is too high as the added electron is in an orbital too close to the parent core. These two energy terms partially cancel each other, leading to a total energy value, and hence an electron affinity value, in good agreement with experiment. This is especially true for large molecules (*i.e.*, hexatriacontane) where the energy due to the excitation or the correlation of the added electron, represents only a small percentage of the total energy.

Although there is no consensus on the dissociation attachment energy values, the tendency for the resonance energy to decrease with increasing carbon chain length is well known and approaches an asymptote with *n*-butane [54]. These trends are confirmed by our DFT calculations (see Tab. III below) which clearly show the decrease in the electron affinity as the chain length increases, and the small variation after butane. This could be interpreted as reflecting a reduction in the influence of the terminal methyl groups on the LUMO as the hydrocarbon chain grows. The semiempirical methods (INDO/2, MNDO, CNDO) show this tendency for the first four alkanes, but remain too negative with increasing chain length. Hartree-Fock theory, as implemented in the code Gaussian94, is too computationally expensive to extend the calculation to long chains. On the other hand, DMol, while too positive for methane is consistent with the experimental estimate for $C_{36}H_{74}$. It would appear that the DMol estimates of the electron affinity

TABLE III Alkanes: *Ab initio* and semiempirical estimates of electron affinities

C_nH_{2n+2}	*Exp**	*DMol* $EA = \Delta E$ *adiabatic* *VWN/DNP/B88/PW*	*DMol* $EA = \Delta E$ *vertical*	*INDO/2* $EA = \Delta E$ *adiabatic*	*MNDO* $EA = \Delta E$ *adiabatic*	*MNDO* $EA = -LUMO$ *vertical*	*CNDO* (17) $EA = -LUMO$ *vertical*	*Gaussian94* $EA = \Delta E$ *adiabatic* 6-311G^{**}/*MP2*
1 methane	−5	−2.87	−2.91	−7.48	−3.57	−4.385	−5.1	−3.76
2 ethane		−2.01	−2.05	−7.15	−3.07	−3.755	−4.5	−3.55
3 propane		−1.95	−1.97	−6.86	−2.72	−3.51	−4.6	−3.37
4 butane		−1.79	−1.8	−6.75	−2.68	−3.404	−4.3	
5 pentane		−1.67	−1.69	−6.66	−2.66	−3.35		
6 hexane		−1.58	−1.58	−6.54	−2.63	−3.311		
7 heptane		−1.51	−1.51	−6.52	−2.61	−3.253		
8 octane		−1.46	−1.45	−6.54	−2.6	−3.21		
9 nonane		−1.42	−1.4	−6.47	−2.61	−3.176		
10 decane		−1.37	−1.36	−6.47	−2.6	−3.15		
13 tridecane		−1.3						
15				−6.45				
20				−6.51	−2.6			
25				−6.45				
30				−6.51				
36 hexa-triacontane	−0.3 ± 0.5	−0.75	−0.75	−6.51				
PE	−0.5 ± 0.5					−3.067		

All values are in eV, *experimental data from (methane) [42], (hexatriacontane) [43] and PE [44]; DE indicates the use of Eqs. (1) (adiabatic) and 2 (vertical).

of alkanes become better (when compared to experimental values) as the chain length increases.

In Table III the results of applying *ab initio* and semiempirical methods to the calculation of the electron affinity of alkanes in vacuum are reported. All the methods produce negative electron affinities, with the CNDO correlation naturally producing a good result for methane.

5. CONCLUSIONS

Density functional theory, as implemented in the code DMol, has been used to calculate the electron affinity of a set of 44 small atoms and molecules. By adding diffuse functions to the basis sets a root mean square deviation from recommended values of 0.1 eV for atoms and 0.3 eV for small molecules has been obtained (for positive electron affinities) in good agreement with previous work on smaller sets of molecules. For molecules with negative electron affinity, DMol (without diffuse functions) appears to produce estimates of electron affinity consistent with the experimental results. Applying DMol to calculations of temporary anion states (or resonances) of linear alkanes (to $n = 36$, where n is the number of carbon atoms) shows a gradual increase in electron affinity which appears to have converged by $n = 36$ to -0.75 eV, consistent with the experimental data for hexatriacontane and polyethylene.

From the results presented above DMol appears to be a useful tool for the calculation of molecular electron affinities. It is particularly suited for large molecules due to its computational speed (especially with respect to other *ab initio* methods). Where the electron affinity is negative DMol appears to provide a good estimate of the electron affinity which, for alkanes, improves in accuracy with increasing molecular weight.

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APPENDIX

The DMol version 96.0/4.0.0 (1996) was used to perform the calculations reported in this article. Parameters have been set as follows:

Functional

Non-local spin density approximation (NLSDA) with the functional of Vosko, Will and Nusair [19] together with the gradient-corrected correlation term of Perdrew-Wang [20] and the gradient-corrected exchange term of Becke [21].

Mesh

The XFINE ($\approx$ 6000 points/atom) parameter has been employed for atoms and molecules, FINE ($\approx$ 3000 points/atom) parameter for alkanes.

SCF Procedure and Geometry Optimization

The density tolerance for SCF was set to 10^{-6}. The DISS algorithm of Pulay was utilized for faster convergence. The geometry optimization convergence criteria were satisfied when the gradient was less than 10^{-4} Hartree/Bohr and when the energy change was less than 10^{-5} Hartree.

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