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On the Gas-Phase Electronic Chemical Potential of Anions

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Abstract: In the process of evaluating intrinsic electronic chemical potentials and related properties of anions in the gas phase, positive values for this quantity often arise. We herein examine in detail this result in terms of computational grounds. At a low level of theory, this result is often obtained, but its origin is mainly traced to the fact that the LUMO energy level is not really converged. Therefore, this outcome may be an artifact of the calculation. We establish the minimum basis set analysis that is to be performed before the electronic chemical potential of charged electron donors, in the absence of medium (solvent) effects, may be safely calculated to yield physically meaningful results. The implications that this result may have on the phenomenological chemical reactivity theory are discussed in detail, mainly those related to the definition of the electron-donating (nucleophilicity) ability of anions in the gas phase. The arguments given are illustrated for a large number of atomic and molecular systems at different levels of theory.

Introduction

The concepts introduced from the density functional theory of chemical reactivity by Parr and Yang¹ have had an enormous impact in the fields of general physical chemistry and physical organic chemistry. A set of recent review works illustrates well this point.^{2–10} However, one of the most relevant achievements of the research work done in this field is that useful concepts like electronic chemical potential, global and local electrophilicity indexes, and electrophilic and nucleophilic Fukui functions have started to be introduced in modern texts of organic chemistry,¹¹ and therefore they are expected to be incorporated in the current language of the physical organic chemist community. Of central importance is the electronic chemical potential μ introduced by Parr and co-workers.^{12–16} This quantity is defined as

$$\mu = \left[\frac{\partial E}{\partial N} \right]_{v(\mathbf{r})} \quad (1)$$

where E is the ground state energy of an N electron atomic or molecular system under the influence of an external potential $v(\mathbf{r})$ due to the compensating nuclear charges in the system. In eq 1, the derivative is taken at fixed $v(\mathbf{r})$. The finite difference approximated expression for μ is given as follows:²

$$\mu \cong - \left[\frac{I + A}{2} \right] \approx \left[\frac{\epsilon_H + \epsilon_L}{2} \right] \quad (2)$$

in terms of the first vertical ionization potential I and electron affinity A , or in terms of the one-electron energies of the frontier molecular orbitals HOMO and LUMO, if the frozen orbital approximation together with Janak's theorem is used.² Extensions to incorporate solvent effects on these properties have been reported for cations and neutrals.^{17,18} It is pertinent for the discussion that follows to remind ourselves that the recommended definitions for I and A for atoms and molecules¹⁹ are

$$S \rightarrow S^+ + e^-; \quad \Delta E = E(S^+) - E(S) = I \quad (3)$$

and

$$S^- \rightarrow S + e^-; \quad \Delta E = E(S) - E(S^-) = A \quad (4)$$

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Table 1. HOMO and LUMO Energy Levels (ϵ_H and ϵ_L , respectively)^a

	compound	ϵ_H	ϵ_L	μ	η	method	reference
1	(NO ₂)C ₆ H ₄ O [−]	−3.27	5.80	1.27	9.06	HF/3-21G(d)	22
2	(COCH ₃)C ₆ H ₄ O [−]	−2.48	7.40	2.46	9.88	HF/3-21G(d)	22
3	HC ₆ H ₄ O [−]	−1.58	9.25	3.84	10.83	HF/3-21G(d)	22
4	(CH ₃)C ₆ H ₄ O [−]	−1.52	9.14	3.81	10.67	HF/3-21G(d)	22
5	(Br)C ₆ H ₄ O [−]	−2.12	8.63	3.25	10.75	HF/3-21G(d)	22
6	(CH ₃ O)C ₆ H ₄ O [−]	−1.66	8.93	3.63	10.59	HF/3-21G(d)	22
7	CH ₃ O [−]	−1.921	12.785	5.432	7.353	HF/6-31G(d)	23
8	CH ₃ CH ₂ O [−]	−2.161	11.954	4.896	7.057	HF/6-31G(d)	23
9	(CH ₃) ₂ CHO [−]	−2.376	11.398	4.511	6.887	HF/6-31G(d)	23
10	(CH ₃) ₃ CO [−]	−2.595	10.819	4.112	6.707	HF/6-31G(d)	23
11	(CH ₃) ₃ CCH ₂ O [−]	−2.643	10.236	3.797	6.439	HF/6-31G(d)	23

^a Corresponding values of electronic chemical potential (μ) and chemical hardness (η) for a series of anions. All values are in eV.

respectively. Experimental evidence shows that, for positively charged species and neutrals, the quantities I and A are in general positive numbers (with some exceptions for A), with $I \gg A$, because the energy required to remove one electron from negative species is less than that needed to take out an electron from a neutral.^{20,21} Therefore, by inspection of the first equality in eq 2, it follows immediately that, for cations and neutrals, the condition $\mu < 0$ is always fulfilled. Unfortunately, experimental data regarding A values for anions are in general not available, and the second approximate expression for the electronic chemical potential given in eq 2 is used instead. In this work, the focus is put on the theoretical estimates of ionization potentials and electron affinities of anions from ab initio methods and their effect on the computed values of the electronic chemical potential in the gas phase.

If Janak's theorem is used, under the general constraint that $\epsilon_L > \epsilon_H$, the following computational cases may arise:

(a) $\epsilon_L > 0 > \epsilon_H$ (normal case: bound HOMO and unbound LUMO states)

(b) $0 > \epsilon_L > \epsilon_H$ (current computational case: bound HOMO and LUMO states)

(c) $\epsilon_L > \epsilon_H > 0$ (less current computational case: unbound HOMO and LUMO states).

We shall now examine them in the following.

Case a: $\epsilon_L > 0 > \epsilon_H$. This case leads to the following possible situations: (i) $\mu > 0$ or (ii) $\mu < 0$. For the former, we have

$$\mu \cong -\frac{(I + A)}{2} \approx \frac{(\epsilon_H + \epsilon_L)}{2} > 0 \quad (5)$$

which entails that $\epsilon_L > -\epsilon_H$. This condition satisfies the constraint $\epsilon_L > \epsilon_H$, for $|\epsilon_L| > |\epsilon_H|$.

For $\mu < 0$, on the other hand, we have

$$\mu \cong -\frac{(I + A)}{2} \approx \frac{(\epsilon_H + \epsilon_L)}{2} < 0 \quad (6)$$

that leads to $\epsilon_L < -\epsilon_H$, a result also consistent with the condition $\epsilon_L > \epsilon_H$, for $|\epsilon_L| < |\epsilon_H|$. Therefore, for the normal case of bound HOMO and unbound LUMO states, the occurrence of positive values of the electronic chemical potential is a possible outcome. We will come back to this problem, and we will show that this statement has only a physical meaning if the LUMO state is conveniently

converged, and that this convergence requires a thorough analysis of the basis set used.

Case b: $0 > \epsilon_L > \epsilon_H$. For $\mu > 0$, we have

$$\mu \cong -\frac{(I + A)}{2} \approx \frac{(\epsilon_H + \epsilon_L)}{2} > 0 \quad (7)$$

which contradicts the hypothesis $0 > \epsilon_L > \epsilon_H$ because it entails that $\epsilon_H > -\epsilon_L$, which is a positive number.

For $\mu < 0$, we have

$$\mu \cong -\frac{(I + A)}{2} \approx \frac{(\epsilon_H + \epsilon_L)}{2} < 0 \quad (8)$$

which entails that $\epsilon_H < -\epsilon_L$, a result consistent with the hypothesis, and is therefore possible. Thus, for the case where both HOMO and LUMO levels are bound states, the only meaningful representation of the electronic chemical potential is the one associated with a negative value.

Case c: $\epsilon_L > \epsilon_H > 0$. This case can never occur, because it leads to a situation where $A < I < 0$, which contradicts the experimental results.

Table 1 summarizes the electronic chemical potential and chemical hardness for a series of anions evaluated in the literature. It may be seen that, independent of the basis set used, Hartree–Fock theory describes the electronic structures of anions within the normal case a discussed above, that is, with bound HOMO and unbound LUMO states. Compounds labeled 1–6 in Table 1 were reported by Mendez et al.²² as part of a theoretical study on the basicity of p-substituted phenolates and the elimination to substitution ratio in the reaction with the reference electrophile p-nitrophenyl bromide. These reactions were analyzed in terms of the empirical HSAB rule so that the focus was put on the hardness (softness) values rather than on the positive values of the electronic chemical potential that result after using the gas-phase one-electron energies of the HOMO and LUMO levels reported therein.²² In order to further analyze the effect of intrinsic positive electronic chemical potentials, and therefore free from solvent complications, we take another benchmark model of acid–base equilibrium of alcohols in the gas phase.²³ Therein, a relationship between relative proton affinities and relative electronic chemical potentials was proposed, using the methoxide anion as a reference for both scales. This model was assumed to correctly describe the gas-phase acidity pattern within the family of alkyl-substituted alcohols in the gas phase, using a thermodynamic

Table 2. HOMO and LUMO Energy Levels (ϵ_H and ϵ_L , respectively)^a

	compound	ϵ_H	ϵ_L	μ	η
1	CH ₃ CO ₂ ⁻	-5.10	5.38	0.14	10.48
2	CH ₃ CH ₂ O ⁻	-2.99	4.38	0.70	7.36
3	CN ⁻	-5.23	6.66	0.72	11.89
4	NO ₃ ⁻	-6.04	7.56	0.76	13.60
5	SH ⁻	-2.55	5.22	1.33	7.77
6	Br ⁻	-3.79	6.94	1.57	10.74
7	OH ⁻	-2.86	6.04	1.59	8.89
8	CH ₃ S ⁻	-2.21	5.52	1.65	7.73
9	CH ₃ O ⁻	-2.74	6.07	1.66	8.82
10	Cl ⁻	-4.08	8.15	2.04	12.24
11	NH ₂ ⁻	-1.26	5.58	2.16	6.84
12	N ₃ ⁻	-2.82	7.97	2.57	10.79
13	F ⁻	-4.83	14.65	4.91	19.47
14	I ⁻	-2.67	21.57	9.45	24.24
15	H ⁻	-0.10	20.11	10.00	20.21

^a Corresponding values of electronic chemical potential (μ) and chemical hardness (η) for a series of anions. All values are in eV.

cycle by combining the proton affinity (PA) of neutrals and anions. In this way, the acid–base equilibria are described in a more balanced way by including the contributions of the neutral and charged species. The variations in proton affinity given by $\Delta PA = PA(RO^-) - PA(CH_3O^-)$ were related to the variations in total electronic chemical potential given by $\Delta\mu_t = \Delta\mu^- - \Delta\mu^N$, where

$$\Delta\mu^- = [\mu(RO^-) - \mu(CH_3O^-)] \quad (9)$$

and

$$\Delta\mu^N = [\mu(CH_3OH) - \mu(ROH)] \quad (10)$$

are the contributions of the change in electronic chemical potential of anions and neutrals, respectively.²³ The values reported in ref 23 show that the contribution of the anions largely outweighs the contribution from the changes in

electronic chemical potential of the neutrals, and therefore, it is the contribution of the alkoxides that drives the proton transfer involved in the gas-phase acid–base equilibria. The alkoxides involved in that study are quoted in Table 1 and labeled as compounds 7–11. This ordering is in agreement with the gas-phase acidity scale of alcohols.²⁴ The inversion of this ordering in the solution phase is well-known,²⁴ and it has been attributed to a differential solvent effect which follows an inverse trend with the anion size.²⁵

Table 2 shows the values of gas-phase electronic chemical potentials for a series of anions involved in gas-phase nucleophilic substitution reactions. The electronic quantities were evaluated in this work at the HF/6-311++G(d,p) level of theory, using the Gaussian 03 program package.²⁶ The addition of diffuse functions is a usual prescription when dealing with anions in the gas phase. This result is useful to show that, even in the case where diffuse functions are incorporated in the calculations, the occurrence of positive values of μ for anions in the gas phase may be a current outcome.

In the process of review of the present material, two reviewers grabbed our attention by suggesting that the numerical data presented in Tables 1 and 2 were insufficient to discuss the sign of the electronic chemical potential of anions in the gas phase, and that the occurrence of calculated positive values for this quantity could be an artifact of the basis set used. One of the reviewers pointed out that the problem should be related to a “definition of electron affinity for system(s) that do not bind another electron”. The definition of the intrinsic electronic chemical potential proposed by Parr et al.¹² entails the energy difference between the neutral and a “metastable” anion. The metastable anion model has been recently addressed in the literature.^{27,28} A second choice is to just put $A = 0$ for anions in the gas phase. The reviewers went on to propose that, within Hartree–Fock theory, the LUMO energy and the electron

Table 3. HOMO and LUMO Energy Levels from Reference HF/6-311++G(d,p) and HF/AUG-cc-pVDZ, HF/AUG-cc-pVTZ, and HF/AUG-cc-pVQZ Levels of Theory

Compound	$\epsilon_H^{(1)}$	$\epsilon_H^{(2)}$	$\epsilon_H^{(3)}$	$\epsilon_H^{(4)}$	$\epsilon_L^{(1)}$	$\epsilon_L^{(2)}$	$\epsilon_L^{(3)}$	$\epsilon_L^{(4)}$
NO ₂ PhO ⁻	-3.270	-3.661	-3.890	-4.052	5.800	3.566	2.192	1.348
CH ₃ COPhO ⁻	-2.480	-3.103	-3.098	-3.366	7.400	3.204	2.872	1.585
(CH ₃) ₃ CCH ₂ O ⁻	-2.643	-3.296	-3.305	-3.586	10.236	3.522	3.136	1.481
NO ₃ ⁻	-6.040	-5.979	-5.984	-5.975	7.560	6.859	6.045	5.520
CH ₃ CO ₂ ⁻	-5.100	-5.094	-5.121	-5.124	5.380	3.982	3.627	3.412
PhO ⁻	-1.580	-2.319	-0.085	-2.305	9.250	3.538	0.117	2.965
CH ₃ PhO ⁻	-1.520	-2.210	-2.199	-2.197	9.140	3.293	2.927	2.738
BrPhO ⁻	-2.120	-2.791	-2.770	-2.766	8.630	3.626	3.252	2.990
CH ₃ OPhO ⁻	-1.660	-2.322	-2.303	-2.588	8.930	3.160	2.849	1.377
(CH ₃) ₂ CHO ⁻	-2.376	-3.177	-3.183	-3.185	11.398	3.934	3.549	3.324
(CH ₃) ₃ CO ⁻	-2.595	-3.387	-3.391	-3.392	10.819	3.833	3.472	3.259
CH ₃ O ⁻	-2.740	-2.801	-2.805	-2.810	6.070	4.345	3.951	3.720
CH ₃ S ⁻	-2.210	-2.257	-2.250	-2.249	5.520	4.165	3.782	3.559
CH ₃ CH ₂ OH ⁻	-2.161	-3.013	-3.016	-3.019	4.380	4.032	3.629	3.406
OH ⁻	-2.860	-2.935	-2.951	-2.959	6.040	5.390	4.861	4.639
N ₃ ⁻	-2.820	-2.853	-2.835	-2.834	7.970	6.460	5.852	5.354
H ⁻	-0.100	-1.223	-1.244	-1.248	20.110	7.666	6.587	6.078
F ⁻	-4.830	-4.931	-4.924	-4.925	14.650	13.850	12.042	10.785
Br ⁻	-3.790	-3.800	-3.792	-3.791	6.940	8.151	6.846	5.913
Cl ⁻	-4.080	-4.096	-4.091	-4.090	8.150	8.850	7.864	7.036
CN ⁻	-5.230	-5.206	-5.207	-5.205	6.660	6.378	5.699	5.209
SH ⁻	-2.550	-2.577	-2.582	-2.581	5.220	4.823	4.285	3.957
NH ₂ ⁻	-1.260	-1.291	-1.312	-1.323	5.580	5.016	4.500	4.235

Table 4. Electronic Chemical Potential and Chemical Hardness from Reference HF/6-311++G(d,p) and HF/AUG-cc-pVDZ, HF/AUG-cc-pVTZ, and HF/AUG-cc-pVQZ Levels of Theory in eV Units

compound	$\mu^{(1)}$	$\mu^{(2)}$	$\mu^{(3)}$	$\mu^{(4)}$	$\eta^{(1)}$	$\eta^{(2)}$	$\eta^{(3)}$	$\eta^{(4)}$
NO ₂ PhO ⁻	1.265	-0.048	-0.849	-1.352	9.070	7.227	6.082	5.400
CH ₃ COPhO ⁻	2.460	0.050	-0.113	-0.891	9.880	6.307	5.969	4.951
(CH ₃) ₃ CCH ₂ O ⁻	3.797	0.113	-0.085	-1.052	12.879	6.818	6.441	5.067
NO ₃ ⁻	0.760	0.440	0.031	-0.227	13.600	12.838	12.029	11.495
CH ₃ CO ₂ ⁻	0.140	-0.556	-0.747	-0.856	10.480	9.076	8.748	8.537
PhO ⁻	3.835	0.610	0.016	0.330	10.830	5.858	0.202	5.270
CH ₃ PhO ⁻	3.810	0.542	0.364	0.271	10.660	5.502	5.126	4.935
BrPhO ⁻	3.255	0.417	0.241	0.112	10.750	6.416	6.022	5.756
CH ₃ OPhO ⁻	3.635	0.419	0.273	-0.606	10.590	5.482	5.152	3.965
(CH ₃) ₂ CHO ⁻	4.511	0.378	0.183	0.070	13.774	7.112	6.732	6.509
(CH ₃) ₃ CO ⁻	4.112	0.223	0.041	-0.066	13.414	7.220	6.864	6.652
CH ₃ O ⁻	1.665	0.772	0.573	0.455	8.810	7.145	6.756	6.530
CH ₃ S ⁻	1.655	0.954	0.766	0.655	7.730	6.422	6.032	5.807
CH ₃ CH ₂ OH ⁻	0.695	0.510	0.307	0.193	7.370	7.045	6.646	6.425
OH ⁻	1.590	1.227	0.955	0.840	8.900	8.325	7.812	7.597
N ₃ ⁻	2.575	1.803	1.508	1.260	10.790	9.313	8.687	8.188
H ⁻	10.005	3.221	2.671	2.415	20.210	8.890	7.830	7.326
F ⁻	4.910	4.459	3.559	2.930	19.480	18.781	16.966	15.709
Br ⁻	1.575	2.175	1.527	1.061	10.730	11.951	10.637	9.704
Cl ⁻	2.035	2.377	1.887	1.473	12.230	12.946	11.955	11.127
CN ⁻	0.715	0.586	0.246	0.002	11.890	11.584	10.906	10.415
SH ⁻	1.335	1.123	0.852	0.688	7.770	7.400	6.867	6.538
NH ₂ ⁻	2.160	1.863	1.594	1.456	6.840	6.308	5.812	5.558

Table 5. Even-Tempered Calculations of HOMO and LUMO Energy Levels Using HF/AUG-cc-pVQZ Level of Theory As Reference in eV Units

compound	$\epsilon_H^{(a)}$	$\epsilon_L^{(a)}$	$\epsilon_L^{(b)}$	$\epsilon_L^{(c)}$	$\epsilon_L^{(d)}$	$\epsilon_L^{(e)}$	$\epsilon_L^{(f)}$	$\epsilon_L^{(g)}$	$\epsilon_L^{(h)}$
CH ₃ O ⁻	-2.810	3.720	2.414	1.622	1.044	0.652	0.596	0.438	0.322
CH ₃ S ⁻	-2.249	3.559	2.382	1.632	1.089	0.995	0.770	0.595	0.460
CH ₃ CH ₂ OH ⁻	-3.019	3.406	2.150	1.483	0.992	0.938	0.731	0.570	0.444
OH ⁻	-2.959	4.639	2.646	2.045	1.498	1.077	0.768	0.545	0.386
N ₃ ⁻	-2.834	5.354	3.161	2.132	1.605	1.069	0.916	0.684	0.510
H ⁻	-1.248	6.078	3.216	2.537	1.963	1.490	1.107	0.807	0.581
F ⁻	-4.925	10.785	5.870	4.283	3.019	2.092	1.441	0.995	0.690
Br ⁻	-3.791	5.913	3.467	2.623	1.911	1.356	0.950	0.663	0.463
Cl ⁻	-4.090	7.036	4.008	2.999	2.164	1.525	1.063	0.740	0.516
CN ⁻	-5.205	5.209	3.180	2.120	1.442	0.973	0.669	0.466	0.357
SH ⁻	-2.581	3.957	2.682	1.837	1.344	0.966	0.689	0.488	0.345
NH ₂ ⁻	-1.323	4.235	2.627	1.793	1.186	0.819	0.557	0.381	0.267

affinity should go to zero if a sufficiently large basis set is used. Both reviewers suggested a more complete discussion about the electron affinities and electronic chemical potential of anions in the gas phase by performing a thorough computational analysis in the infinite basis set limit, by adding diffuse functions until the LUMO energy level is converged. In order to perform such an analysis, we have chosen a modification of the even-tempered basis set approach, which consists of adding, in a systematic way, more and more diffuse functions of each symmetry to a well-established extended basis set like the family of aug-cc-pvNZ (with $N = 2, 3, 4, 5, \dots$) bases.²⁹

The procedure used to converge the HOMO and LUMO energy levels was as follows: First of all, we considered the series depicted in Table 3 and used the calculation with the reference HF/6-311++G(d,p) wave function quoted in Table 3 as $\epsilon_H^{(1)}$ and $\epsilon_L^{(1)}$. Then, the structures of anions were reoptimized using the Dunning–Huzinaga basis set (aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ). The HOMO and LUMO energy levels obtained from these calculations are quoted in Table 3 as $\epsilon_H^{(2)}$, $\epsilon_L^{(2)}$, $\epsilon_H^{(3)}$, $\epsilon_L^{(3)}$, $\epsilon_H^{(4)}$, and $\epsilon_L^{(4)}$, respectively.

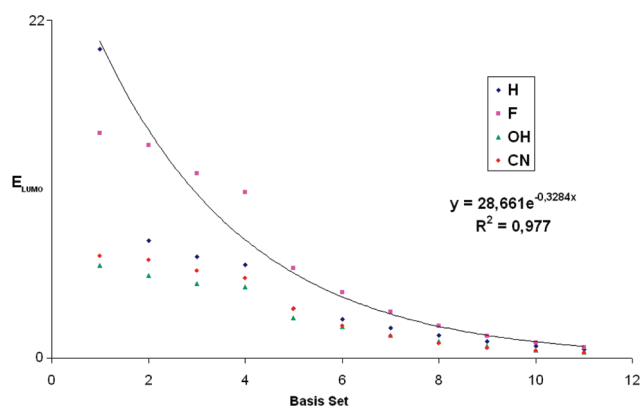
Note that the HOMO level is converged more rapidly than the LUMO level by increasing the basis set. Table 4 summarizes the calculated electronic chemical potential and chemical hardness using the numerical data of Table 3, using eq 2. It may be seen that increasing the basis set results in the inversion of the sign of the electronic chemical potential for 6 out of 23 anions within the series.

Some of the nonconverged anions quoted in Table 4 were selected for further analysis. They are displayed in Table 5. Note that this series included the harder anions that are expected to be more difficult to converge. This series was subjected to even-tempered basis set calculations. Specifically, the procedure consists of taking the geometry obtained at the HF/AUG-cc-pVQZ level of theory, and the exponents of the basis set were reduced following a geometric progression $[(1)/(2)]^n$ for $n = 1-7$. The results are quoted in Table 6 as $\epsilon_H^{(b)}$, $\epsilon_L^{(b)}$, $\epsilon_H^{(c)}$, $\epsilon_L^{(c)}$, $\epsilon_H^{(d)}$, $\epsilon_L^{(d)}$, $\epsilon_H^{(e)}$, $\epsilon_L^{(e)}$, $\epsilon_H^{(f)}$, $\epsilon_L^{(f)}$, $\epsilon_H^{(g)}$, $\epsilon_L^{(g)}$, $\epsilon_H^{(h)}$, and $\epsilon_L^{(h)}$, respectively.

Note that, following the even-tempered procedure, the LUMO energy level dramatically diminishes, yet the complete convergence limit has not been yet attained. However,

Table 6. Even-Tempered Calculations of the Electronic Chemical Potential Using a HF/AUG-cc-pVQZ Levels of Theory As Reference^a

compound	$\mu^{(a)}$	$\mu^{(b)}$	$\mu^{(c)}$	$\mu^{(d)}$	$\mu^{(e)}$	$\mu^{(f)}$	$\mu^{(g)}$	$\mu^{(h)}$
CH ₃ O ⁻	0.455	-0.212	-0.608	-0.897	-1.093	-1.121	-1.200	-1.258
CH ₃ S ⁻	0.655	0.057	-0.318	-0.590	-0.636	-0.749	-0.837	-0.904
CH ₃ CH ₂ OH ⁻	0.193	-0.435	-0.769	-1.021	-1.048	-1.151	-1.232	-1.295
OH ⁻	0.840	-0.161	-0.462	-0.735	-0.945	-1.098	-1.208	-1.287
N ₃ ⁻	1.260	0.163	-0.351	-0.615	-0.883	-0.959	-1.076	-1.162
H ⁻	2.415	0.980	0.639	0.353	0.118	-0.072	-0.221	-0.334
F ⁻	2.930	0.472	-0.322	-0.953	-1.417	-1.742	-1.965	-2.117
Br ⁻	1.061	-0.162	-0.584	-0.940	-1.217	-1.421	-1.564	-1.664
Cl ⁻	1.473	-0.041	-0.546	-0.963	-1.282	-1.514	-1.675	-1.787
CN ⁻	0.002	-1.013	-1.543	-1.882	-2.116	-2.268	-2.370	-2.424
SH ⁻	0.688	0.049	-0.373	-0.620	-0.809	-0.947	-1.047	-1.118
NH ₂ ⁻	1.456	0.643	0.225	-0.078	-0.262	-0.391	-0.476	-0.533

^a Units are eV.**Figure 1.** LUMO energy versus basis set size for hydride ion.

at this limit, the electronic chemical potential has begun to reach negative values, see Table 6.

In order to get an estimate of the convergence limit for the LUMO levels of anions quoted in Table 6, a fit of the LUMO levels against the order of the progression was performed. The results are summarized in Figure 1. It may be seen that, for $n = 12$ in the even-tempered curve, one can safely consider that the LUMO level of anions will go to zero in the infinite basis set limit, as suggested by the reviewers. This result is also consistent with a choice of $A = 0$ for the electron affinity of negatively charged systems that do not bind an extra electron.

In summary, the calculation of the electronic chemical potential and related properties of anions in the gas phase absolutely demands a thorough computational analysis in the infinite basis set limit. Any calculation using the Pople basis set even including polarization function may lead to the spurious result that the electronic chemical potential of anions may become a positive number. Our results suggest that the minimum level of theory must at least include the aug-cc-pVQZ basis set together with an even tempered calculation as the one described here for $n = 3$.

The present results strongly suggest that, for anions, the value $A = 0$ is a reasonable approach for the electron affinity of anions. With this result at hand, the electronic chemical potential of anions in the gas phase would approach the limit $\mu = -I/2 \approx \epsilon_H/2$. This result is reasonable if we consider that anions in the gas phase are more likely expected to

behave as electron donors (nucleophiles), and in this sense, the intrinsic nucleophilicity of charged electron donors appears related to the ionization potential, as suggested by one of us.^{30,31}

Concluding Remarks

We have demonstrated herein that the occurrence of positive values of the electronic chemical potential for anions in the gas phase is a possible outcome in ab initio calculations that use the Pople basis set, even including polarization functions. A thorough computational analysis shows that this result may be spurious if the convergence of the LUMO level is not completed. The results obtained here strongly suggest that a reasonable approach for the electron affinity of singly charged electron donors is $A = 0$. This choice is consistent with a model of nucleophilicity in the gas phase which may be simply related to the first ionization potential.

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