# Proton Affinities Calculated by Traditional *ab initio* Approaches and by Density Functional Methods.

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**Abstract:** Proton affinities for ethanol, formate, formic acid, methanol and methylamine calculated by *ab initio* Hartree-Fock and MP2 approaches, and various Density Functional Theory (DFT) methods are compared. Local Spin Density (LSD) calculations did not produce satisfactory results. However, Becke/Perdew nonlocal gradient correction applied as a perturbation to the LSD energy, or in a self-fconsistent fashion dramatically improve calculated affinities yielding values of the same quality as *ab initio* MP2 approach.

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# Introduction

Protonation reactions, i.e., $A + H^+ \rightarrow AH^+$, are among the most important in chemistry and biology. Protonation/deprotonation is the first step in many fundamental chemical rearrangements and in most enzymatic reactions. Two quantities are used to characterize the ability of a molecule in the gas phase to accept a proton. The gas phase basicity is the negative of the free energy change associated with the reaction. The more frequently used index, the proton affinity, is the negative of the enthalpy change at standard conditions. Experimental determination of these parameters is not easy (for an excellent review on this topic see Dixon and Lias[1]), and with the phenomenal growth in computer power in recent years, much attention has been given to the possibility of calculating these parameters by quantum methods. *Ab initio* approaches are very successful in providing reliable values of proton affinities and gas phase basicities for small molecules even at lower levels of theory[2]. However, due to computational expense, application of *ab initio* methods to the estimation of proton affinities is still impractical for larger molecules. Semiempirical methods such as AM1, MNDO and PM3, are not consistently reliable in calculations of proton affinities as shown by Ozment and Schmiedekamp[3].

The recent progress in the Density Functional Theory (DFT) approaches (for review see refs 4-6) make this method another candidate for reliable calculation of proton affinities, however, the performance of the method in this field is still mostly untested. This prompted us to analyze its performance on a few representative molecules spanning a wide range of proton affinity values.

DFT methods are computationally less demanding than correlated *ab initio* approaches and formally scale with the size of the molecule as $N^3$ or $N^4$, depending on implementation. For the the simplest Hartree-Fock *ab initio* approach the scaling is $N^4$. Moreover, the advantage of DFT methods is that they should in principle include electron correlation energy via the correlation/exchange potential, while the Hartree-Fock approach by definition does not include this component of energy. The simplest of the routinely-used *ab initio* correlated approaches, based on the second order many body perturbation theory, MBPT(2) (frequently called second order Møller-Plesset theory – MP2), recovers only a portion of the correlation energy and scales as $n \times N^4$ ($n$ is the number of occupied molecular orbitals). The major weakness of DFT approaches is that the exact mathematical form of the exchange-correlation potential is not known. For that reason approximations are used. The most popular is the Local Spin Density (LSD) approximation, which simply assumes that the exchange-correlation potential dependence upon charge density is represented by the functional form found for the homogenous electron gas. This approximation works well in many cases; however, it suffers from severly underestimating electron exchange[29] and overestimating the correlation energy[30]. Appropriate corrections to the local density approximation are therefore sought, and several of such schemes already exist[42,43].

## Computational Methods

Proton affinity $P(\mathrm{A})$ is defined as the negative of the molar enthalpy change at 298.15 K ($-\Delta H_{\mathrm{Rn}}$) for the reaction $\mathrm{A} + \mathrm{H}^+ \rightarrow \mathrm{AH}^+$, or in the case of anions, $\mathrm{A}^- + \mathrm{H}^+ \rightarrow \mathrm{AH}$. To calculate these values from theory for gas phase reactions we may, in most cases, obtain adequate results assuming ideal gas behaviour: $\Delta H_{\mathrm{Rn}} = \Delta E_{\mathrm{Rn}} - RT$. Assuming that there is only one conformer present, the energy $E(T)$ of a mole of gas consisting of nonlinear polyatomic molecules can be approximated as[33]:

$$E(T) = \underbrace{\frac{3}{2}RT}_{E^{trans}} + \underbrace{\frac{3}{2}RT}_{E^{rot}} + \underbrace{ZPE + E'^{vib}(T)}_{E^{vib}} + E^{elec} \tag{1}$$

$$ZPE = \sum_{i=1}^{3n-6} \frac{Nh\nu_i}{2} \tag{2}$$

$$E'^{vib}(T) = \sum_{i=1}^{3n-6} \frac{Nh\nu_i}{e^{Nh\nu_i/RT} - 1} \tag{3}$$

where $n$ denotes the number of atoms in the molecule, $ZPE$ is the *zero point energy*, $E'^{vib}(T)$ represents the temperature dependent portion of vibrational energy, $\nu_i$ are the calculated vibrational frequencies and $E^{elec}$ is the electronic energy[7]. The change in the energy occuring during protonation of 1 mole of gas at 298.15°K, $\Delta E_{\mathrm{Rn}} = E_{\mathrm{AH^+}}(298.15°\mathrm{K}) - E_{\mathrm{A}}(298.15°\mathrm{K}) - E_{\mathrm{H^+}}(298.15°\mathrm{K})$, will therefore consist of the following components:

$\Delta E^{rot}_{\mathrm{Rn}}$ – the change in rotational energy upon conversion of the reactants to the product. Since a proton does not possess rotational kinetic energy, this term is nonzero only if the protonated molecule has a different fundamental shape than the parent one (e.g., when A is linear and $\mathrm{AH^+}$ is nonlinear). In our case, all parent and protonated molecules are nonlinear, hence, $\Delta E^{rot}_{\mathrm{Rn}} \equiv 0$.

$\Delta E^{trans}_{\mathrm{Rn}}$ – the change in energy associated with translational degrees of freedom. Since the proton on the left hand side of the equation brings $\frac{3}{2}RT$, the net $\Delta E^{trans}_{\mathrm{Rn}} = -\frac{3}{2}RT$; i.e., for 298.15 K $\Delta E^{trans}_{\mathrm{Rn}} \approx 0.88873249$ kcal/mol.

$\Delta E^{vib}_{\mathrm{Rn}}$ – the change in energy associated with internal vibrations of reactants and products. Only the change in the *zero point energy*, $\Delta ZPE$ is significant. The $\Delta E'^{vib}$ is usually much less then 1 kcal/mol at room temperatures (i.e., much smaller than the experimental error) and is included here only for completeness.

$\Delta E^{elec}_{\mathrm{Rn}}$ – the change in the electronic energy upon reaction. In our case it is the difference between ground state energies (electronic + nuclear) taken from quantum calculations with full geometry optimization for the protonated and parent molecules. The ground state energy of a proton is zero in this formulation.

Combining the above, the following expression for proton affinity was used in actual computations:

$$P(\mathrm{A}) = -\Delta E^{elec}_{\mathrm{Rn}} - \Delta ZPE - \Delta E'^{vib} + \frac{5}{2}RT \tag{4}$$

The values of $E^{elec}$ and the vibrational frequences $\nu_i$ were obtained from quantum calculations. Programs Gaussian90[8] and ACES2[9] were used for traditional *ab initio* calculations. The original double-zeta basis set of Dunning/Huzinaga[10] (9s,6p/4s) $\longrightarrow$ (6111,411/31) was augmented with polarization functions: d-type on C, N, O with exponents equal to: 0.8, 0.8, and 0.9 respectively, and p-type with an exponent equal to 1.0 for H. Two sets of *ab initio* calculations were performed. DH6D set used cartesian gaussians (i.e., six d-type functions) and the DH5D[11] set used five d-type functions with the angular part represented by spherical harmonics. These DZP basis sets had similiar characteristics to the basis sets we used in our DFT calculations. The RHF and MP2 calculations were also performed for formic acid and its anion with a DH6D basis set augmented with diffuse s-type and p-type functions (with exponent 0.0845[12]) on oxygen atoms. It is well known that adding diffuse functions on nonhydrogen atoms dramatically improves results for proton affinities[13] though it is less important for molecular geometry. This basis set is referred to later as DH6D$^{(+)}$.

The *ab initio* results were compared with those obtained from DFT calculations performed with the programs: DGauss[14], DMol[15] and an academic version of deMon[16]. The DGauss and deMon programs use the LSD potential developed by Vosco *et al.*[17] while DMol incorporates the Barth and Hedin LSD potential[18].

Basis sets of double-zeta quality with polarization functions were used in all DFT programs. In DMol, the DNP (Double Numerical with Polarization) basis set included with the program was selected. The basis sets in this program are given numerically as cubic spline functions. The 300 radial points spaning a range from nucleus to an outer distance of 10 bohrs is a default. The angular portion of each basis function corresponds to the appropriate spherical harmonic. The DGauss and deMon basis functions are analogous to those widely used in traditional *ab initio* calculations, i.e., they are represented analytically by a combination of primitive gaussian functions; however, they have been reoptimized for the DFT calculations[20]. For DGauss and deMon DZVP atomic basis set and A2 auxiliary fitting set was used for 1st row atoms and DZVPP/A1 set for hydrogens. The contraction pattern for the atomic basis set was (9s,5p,1d/5s,1p) $\longrightarrow$ (621,41,1/41,1). In other words, for 1st row atoms there were three s-type basis functions combining six, two, and one gaussian primitives, respectively; two sets of p-type basis functions containing four and one primitives, and a single primitive for each of the six d-type polarization functions[19,20]. For hydrogens two s-type functions combining four and one gaussian primitives, and p-type polarization functions consisting of one gaussian were used as a basis set.

Beside atomic basis set, in DGauss and deMon, auxiliary sets of functions are used to fit charge density and exchange-correlation potential[20]. For each atom there is one set for fitting density and another set for fitting exchange-correlation potential. The sets consist of uncontracted s-type gaussians and a few groups of s, p, and d-type cartesian gaussians sharing the same exponent. The composition of these sets is denoted as (A,B;C,D), where A,B pair specifies that A s-type gaussians, and B groups of spd gaussians were used for fitting density, and C s-type gaussians and D groups of spd gaussians were used to fit exchange-correlation potential. The A2 auxiliary set was denoted (4,4;4,4), while the smaller A1 set used for hydrogens was (3,1;3,1).

Starting geometries for molecules were obtained from model building with Sybyl[21] using previous computational results[22,23] and experimental data[24–26].

Geometries of protonated molecules were obtained by placing a proton at position of the lone electron pair of the accepting atom. The X–H bond lengths from the corresponding unprotonated molecules were used for these new bonds as starting values. These geometries were then fully optimized within given method. It was absolutely necessary since these final geometries were used for normal modes and vibrational frequency calculations. Atom numbering used throughout this paper is shown in Figure 1 which was produced with the MindTool software[27].

**Figure 1**

Ab initio geometry optimizations were performed in DIRECT SCF mode with Gaussian90, and the resulting geometries were used with ACES2 for vibrational frequency and normal mode calculations. ACES2 computes normal modes and frequencies from the analytical Hessian for RHF and MP2 calculations. We also performed geometry optimizations at the MP2 level (full core) with Gaussian90 in an analogous manner, followed by frequency calculations with ACES2. In the MP2 case we used the RHF-optimized geometries as starting data.

The DFT calculations with both DGauss and DMol were carried out with full geometry optimization at the Local Spin Density (LSD) level. Geometry optimizations with nonlocal gradient corrections were performed with deMon. Geometry optimization was followed by frequency calculations. For all DFT codes the Hessian needed for frequency and normal modes evaluation was calculated from analytical energy gradients by finite differences with a step of 0.01 bohr.

Integration grid in DGauss and deMon was of similar quality (MEDIUM and FINE respectively). In DMol the FINE integration grid density was used and the the maximum angular momentum number (LMAX) of the multipolar functions used to analitically fit electron density and exchange-correlation potential was 2 for hydrogens and 3 for other atoms.

Nonlocal density gradient corrections to the LSD energies were not available in this version of DMol. The version of DGauss used by us provided for single-point nonlocal gradient corrections to LSD energies, while the deMon program offered gradients of nonlocal gradient corrections, i.e., provided for geometry optimization at this level. Based on our previous experience[28], we chose the Becke[29] functional for the exchange and Perdew[30] functional for the correlation potential, which we label Becke-Perdew corrections. The

Becke-Perdew corrections were shown to improve results compared to LSD approximation[31]. Since gradients of gradient-corrected energies could not be calculated with this version of DGauss, single-point corrected energies were calculated for the LSD-optimized geometries and vibrational contributions to proton affinities were assumed to be the same as for the LSD. For deMon, the fully-consistent LSD and NLSD results are reported.

# Results and Discussion

## Geometries

Structural parameters obtained by different methods are compared in Tables I–IV. Since geometries resulting from DH6D and DH5D basis sets are practically identical, only results of RHF and MP2 calculations for DH6D set are reported.

It is well known that bond lengths calculated by the Hartree-Fock method are usually too short compared to experimental values, while the corresponding MP2 values[2] are much closer to reality. It was also supported by these calculations and clearly expressed for the polarized C–O and O–H bonds.

This effect was smaller for C–N and N–H bonds and quite small for C–C and C–H bonds. Bond lengths from DFT bracket *ab initio* values on both sides. Bonds involving hydrogen (C–H, N–H or O–H) which resulted from LSD calculations are the longest of all, and the effect is most visible for the O–H bonds and the smallest for the C–H bonds. The situation is opposite for bonds between the carbon atom and another 1st row element. These bonds calculated with LSD are the shortest of all methods and the magnitude of this effect follows bond polarity.

Becke-Perdew corrections substantially improve bond lengths. The H–X bonds are now shorter than for the case of uncorrected LSD. The C–X bonds with Becke-Perdew corrections are longer than their LSD counterparts. This brings bond lengths calculated with Becke-Perdew corrections to a much closer agreement with experimental and MP2 values.

Valence angles usually follow the known trend in which the angle between shorter bonds tends to be larger, while angle between overestimated bonds is frequently smaller than it should be. This trend is evident if one compares HF and MP2 results. It is also pronounced for H–X–Y angles, which are usually too small for LSD calculations due to the underestimation of X–Y bond length.

Generally, the structural parameters calculated by different methods are similar. Larger discrepancies are visible for torsional angles in ethanol and protonated ethanol. It is not surprising, however, since the potential energy surface for torsional angles pivoted on the C–O bond of ethanol is very flat, and it is still being debated if the minimum energy of ethanol corresponds to a gauche or trans conformation.

## Proton Affinities

Total energies calculated by different quantum approaches are listed in Table V.

## Table V

Direct comparison of absolute total energies calculated by different methods used in this work is only possible among the results obtained by the same program. For *ab initio*, as expected, the inclusion of six d-type polarization functions (in the DH6D basis set), compared with five pure d-type functions (in the DH5D basis set) lowers the calculated energy. Using six cartesian d-type gaussians is equivalent to using the set of five pure functions of d-type augmented with a 3s-type (i.e., $Nr^2exp[-\alpha r^2]$) function. This energy change is negligible for our RHF calculations (on average 0.00060 hartree, i.e., ≈0.38 kcal/mol), however, this change is roughly 10 times larger (on average 0.0059 hartree, i.e., ≈3.7 kcal/mol) for MP2 calculations. This reflects the fact that polarization functions contribute substantially to low-lying virtual orbitals, and the contamination with the 3s orbital brought by combination of six cartesian d-type functions is expressed much more strongly in correlated methods than at the RHF level. On the other hand, the difference between corresponding MP2(5d) and MP2(6d) energies is essentially identical for the parent and protonated molecule thus, this basis set modification does not significantly affect the electronic energy contribution, $\Delta E^{elec}_{\mathrm{Rn}}$, to the calculated proton affinity. This should be expected since the parent and the protonated molecule have the same number of "heavy" atoms whose basis sets contain d-type functions and they differ only in the number of hydrogen atoms.

The effect of adding Becke-Perdew corrections to the LSD energy can be examined for DGauss and deMon calculations. It is known that LSD approximation tends to grossly overestimate correlation energy (frequently as much as 100%) while it underestimates electron exchange energy by as much as 10%[6]. Both, the exchange and the correlation energy, are negative but typically the magnitude of electron exchange energy is of several orders of magnitude larger than the correlation energy for the same system. Therefore, the magnitude of the 10% correction to the exchange energy is typically larger than the magnitude of the correlation energy. For this reason, NLSD corrected energies are lower than the corresponding LSD energies.

DMol uses five d-type functions) while DGauss and deMon use six cartesian gaussians as d-type functions. Judging from *ab initio* results, this difference should not have any substantial impact on the calculated proton affinities.

The changes in the ground state electronic energies on protonation, $\Delta E^{elec}_{\mathrm{Rn}}$, are ordered as: DMol $<$ DGauss(LSD) $\approx$ deMon(LSD) $<$ DGauss(NLSD) $\approx$ deMon(NLSD) $<$ MP2(6d) $\approx$ MP2(5d) $<$ RHF(6d) $\approx$ RHF(5d). This finding suggests that the LSD approximation generally underestimates electronic energy changes on protonation, and gradient (NLSD) corrections bring the results significantly closer to the MP2 values.

The DH5D and DH6D basis sets are far from optimal for calculations of proton affinities since they do not include diffuse s and p-type functions[13]. It is dramatically pronounced in the calculated energies for anions. However, they were chosen here for comparison with DFT calculations. Inclusion of diffuse functions is absolutely required[2,12,32] for meaningful calculations of electronic energy for anions by *ab initio* methods.. To illustrate the effect of diffuse functions, we performed RHF and MP2 calculations for formate anion, and the corresponding neutral acid with DH6D basis set augmented with diffuse s-type and p-type functions on oxygen atoms. As expected, this led to a substantial lowering of electronic energy for the formate anion, while the effect was much smaller for the neutral acid, i.e., the $\Delta E^{elec}_{\mathrm{Rn}}$ was significantly smaller for the basis sets including diffuse functions. Surprisingly, the DFT methods seem less sensitive to the lack of diffuse functions. This apparent insensitivity of the DFT calculations to the inclusion of diffuse functions may be explained by the fact that the underlying quantity in the DFT calculation is the charge density. Diffuse functions do not contribute substantially to the occupied molecular orbitals, and the charge density is the sum of one-particle densities derived from the corresponding occupied orbitals. This reasoning is indirectly supported by our *ab initio* results. The HF energy for the formate, is substantially less affected by adding diffuse functions (0.0110 hartree) than the MP2 energy (0.0222 hartree). The energies of formic acid calculated with and without diffuse functions differ by 0.0032 and 0.0090, for HF and MP2; respectively.

Table VI collects zero point energies ($ZPE$) derived from calculated vibrational frequencies by eq 2, and the temperature-dependent portion of vibrational enthalpies, $E'^{vib}$, computed from eq 3 for the molecules studied. All values of $E'^{vib}$ are small for molecules of this size, in our case on the order of 1 kcal/mol or less. Consequently, the differences between $E'^{vib}$ values for the parent and protonated molecules are negligibly small compared to the experimental error in proton affinity measurements. For larger molecules $\Delta E'^{vib}$ can also be safely omitted in proton affinity calculations since the largest contributions to $E'^{vib}$ come from the lowest frequency vibrations (e.g., torsions around single bonds) and these are for the most part not substantially affected by protonation.

## Table VI

The value of $ZPE$ is proportional to the sum of vibrational frequencies, and therefore it is primarily affected by larger frequences (e.g., bond stretching and bending vibrations). The differences in $ZPE$ for protonated and parent molecule is therefore not small and in our case approaches 10 kcal/mol. Protonation results in the formation of a new covalent X—H bond and also affects geometry and strength of vicinal bonds. For that reason, $\Delta ZPE$ must be accounted for in proton affinity calculations. Also, systematic over- or under-estimation of frequencies will bias the value of $ZPE$ in the same direction. Moreover, it should be noted that $ZPE$ in our case is calculated within the harmonic approximation. Experimental frequencies available in the literature for our series of molecules are not corrected for anharmonicity, and therefore, direct comparisons with experimental values of $ZPE$ were not attempted.

The magnitudes of calculated $ZPE$'s in our series of molecules are ordered as: DMol $\approx$ DGauss(LSD) $\approx$ deMon(LSD) $\approx$ deMon(NLSD) $<$ MP2(6d) $\approx$ MP2(5d) $<$ RHF(6d) $\approx$ RHF(5d). RHF frequences are usually larger than experimental (even if measured frequencies are converted to harmonic ones) and therefore the RHF calculated $ZPE$'s are too large[2]. The MP2 calculated frequencies are in much better agreement with experiment, though in general they are also slightly higher than measured harmonic frequencies[2]. This effect is clearly visible in stretches along polar X—H bonds. Since

LSD calculated zero point energies are slighlty smaller than MP2 calculated ones, they exhibit the plausible trend. RHF and MP2 calculations with the DH6D$^{(+)}$ basis set for formic acid, and the corresponding anion, produced $ZPE$'s very similar to the DH6D basis set. The major contribution to error in proton affinities of anions calculated with basis sets lacking diffuse functions is therefore from the electronic energies.

Proton affinities were calculated from eq 4. The values of calculated gas phase proton affinities together with the experimental values are collected in Table VII. The errors in experimental values are roughly 2 kcal/mol for affinities within 167–204 kcal/mol range and the error gets much larger outside this range due to the lack of adequate reference proton affinities[34].

## Table III

The RHF(6d) and RHF(5d) calculated proton affinities are practically identical. In our series of molecules they are all too large compared to experimental values. Overestimation of proton affinities at the RHF level is well illustrated by other authors for similar molecules[22,2,3,35,36]. This trend in RHF calculations is mainly due to the overestimated $\Delta E^{elec}_{\mathrm{Rn}}$, however, $\Delta ZPE$ is usually also exaggerated since the calculated frequency of the newly formed X—H bond is too large. The MP2 results are practically identical for MP2(6d) and MP2(5d) cases, and are in substantially better agreement with experimental values. As was mentioned above, adding diffuse functions on oxygen dramatically improves the calculated proton affinity for the formate anion.

The proton affinities calculated within the LSD approximation are substantially smaller than the experimental values. For our series of molecules, LSD underestimates $\Delta E^{elec}_{\mathrm{Rn}}$. Proton affinities calculated with DGauss(NLSD) and deMon(NLSD) are in excellent agreement with the experimental values. They are even slightly better ($\sigma_{DGauss(NLSD)} = 2.4$ kcal/mol, $\sigma_{deMol(NLSD)} = 2.3$ kcal/mol) then those from MP2 calculations ($\sigma_{MP2(6d)} = 2.6$ kcal/mol when the result obtained with diffuse basis functions was used for formate) and much better than the ones from RHF calculations ($\sigma_{RHF(6d)} = 4.4$ kcal/mol).

It seems that for this particular series of molecules it does not matter if gradient corrections were applied perturbationally to the LSD energy (at LSD optimized geometry) or if they were introduced in a self-consistent way during geometry optimization. This may, however, be fortuitous due to the fact that C—X bonds are slightly shorter and X—H and C—H slightly longer than for the corresponding NLSD calculations. It may provide for some cancellation of errors which results in similar overall values of affinities.

## Concluding Remarks

We have shown that the DFT methodology is a good candidate for routine calculations of proton affinities. However, it is evident that the nonlocal gradient corrections have to be used to correctly estimate the change in electronic energy of protonation. The results obtained with Becke-Perdew corrections applied perturbationally or in a self-consistent manner are of MP2 quality but require much less computation. Moreover, since DFT methods scale formally with molecular size as $N^3$ (compared to $N^5$ for MP2 *ab initio* approach) they can be applied to much larger molecules.

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