Supporting Information

Validation of Koopmans' Theorem for Density Functional Theory Binding Energies

Noèlia Pueyo Bellafont,[1] Francesc Illas[1*] and Paul S. Bagus[2*]

1) *Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain*

2) *Department of Chemistry, University of North Texas, Denton, TX 76203-5017, USA.*

(*) Corresponding authors:

Paul S. Bagus, +1 512 502 9397 and Paul.Bagus@unt.edu

Francesc Illas, +34 934 021 229 and francesc.illas@ub.edu

We have compared our theoretical results for the N(1s) BE's with the XPS experimental results given in the review of the BE's for gas phase atoms and molecules by Bakke et al. [1] For 9 out of our 15 test molecules, this review [1] gives more than one XPS measurement of the N(1s) BE's. In all cases but one, HCN, the differences for the different values are small and usually within the uncertainty of ±0.1 eV that we have used for the experimental data in Tables I and III. In these cases, we have used the average value of the N(1s) BE's for the entries in Tables I and II. For HCN, the two N(1s) BE's given differ by 0.7 eV which is significantly outside of the accuracy of XPS measurements; see, for example, Refs. [2-3]. The smaller BE of 406.13 eV from an unpublished PhD. Thesis. see Ref. [1], is much less consistent with our theoretical data than the larger published BE of 406.8 eV. [1] In particular, the smaller N(1s) BE would lead to the HF BE(ΔSCF) being larger than experiment. Although this anomalous sign of error for HF BE(SCF) may occur, [4] it is normally not expected. For these reasons, for HCN we have used the larger BE in the Bakke et al. review [1] rather than the average of the two values.

Density Functional Theory, DFT, calculations with the Kohn-Sham implementation and the hybrid B3LYP functional [5] have been carried out to determine the molecular structure of the molecules in the validation set. These are: ammonia (NH_3), methylamine (CH_3NH_2), aniline ($C_6H_5NH_2$), N-methylaniline ($C_6H_5NHCH_3$), N- N-dimethylaniline ($C_6H_5N(CH_3)_2$), cyanobenzene (C_6H_5CN), pyridine (C_5H_5N), pyrrole (C_4H_4NH), hydrogen cyanide (HCN), acetonitrile (CH_3CN), dimethylamine ($(CH_3)_2NH$), ethylamine ($CH_3CH_2NH_2$), diethylamine ($(CH_3CH_2)_2NH$), trimethylamine ($(CH_3)_3N$), propylamine ($CH_3CH_2CH_2NH_2$), N,N-dimethylbenzene-1,4-diamine (p-$(CH_3)_2NC_6H_4NH_2$), and 4- cyanoaniline (p-CN-$C_6H_4NH_2$). Note that the two latter have two different types of N atoms. These geometries are then used for both the DFT and HF calculations of the N(1s) BE(KT) and BE(ΔSCF).

To avoid errors arising from the use of basis sets which are not at the basis set limit, all calculations have been carried out using near Hartree-Fock basis sets including polarization functions. For the C and N atoms, we used the Partridge (14s, 9p) fully uncontracted set [6] augmented by a d function set taken from the pVTZ set [7-8] whereas for H we used a (5s) uncontracted basis set with all exponents taken from the VTZ basis [9] augmented with a p function set with 0.8 exponent as suggested by Ahlrichs. [10-11] As explained in the main text the use of uncontracted basis sets is necessary for the N atom basis set in order to have comparable accuracy for the ground, initial state and for the N(1s) hole states. For consistency in the construction of the basis sets, we also uncontracted the C and H basis sets as well as the N basis set. All basis sets have been downloaded [11] from the EMSL Basis Set Exchange. [12-13]

The optimization of the geometry of the ground states of the neutral molecules was obtained with the B3LYP DFT functional by locating an energy minimum in the potential energy surface through appropriate frequency analysis. All calculations have been carried out using the GAMESS-06 [14-15] and CLIPS [16] codes. The HF and the KS orbitals are all spin-restricted where the where the spatial parts of the α and the β spin orbitals are identical; this is especially relevant for the N(1s) hole configurations.

In Tables S1 and S2 we give the total energies of the initial and final, N(1s) hole, configurations for the HF and KS results, respectively. These energies are useful for anyone wishing to reproduce our calculations.

Table S1. HF total energy for initial and N(1s) ionized state of the molecules included in the validation set at the B3LYP optimized geometry.

	Total Energy (a.u.)	
Molecule	Initial State	Final State
NH_3	-56.218814	-41.326329
CH_3NH_2	-95.254843	-80.381467
$C_6H_5NH_2$	-285.833186	-270.953781
$C_6H_5NHCH_3$	-324.872094	-310.003723
$C_6H_5N(CH_3)_2$	-363.905699	-349.046213
C_6H_5CN	-322.543886	-307.672607
C_5H_5N	-246.778231	-231.921350
C_4H_4N	-208.885371	-193.974663
HCN	-92.909643	-77.967773
CH_3CN	-131.975432	-117.078700
$(CH_3)_2NH$	-134.294493	-119.433909
$CH_{3C}H_2NH_2$	-134.306403	-119.440234
$(CH_3CH_2)_2NH$	-212.391065	-197.545306
$(CH_3)_3N$	-173.335723	-158.483662
$CH_3CH_2CH_2NH_2$	-173.354701	-158.490684
p-$(CH_3)_2NC_6H_4NH_2$ – N from $N(CH_3)_2$	-418.954458	-404.085617
p-$(CH_3)_2NC_6H_4NH_2$ – N from NH_2	-418.954458	-404.103504
p-CN-$C_6H_4NH_2$ – N from CN	-377.600286	-362.748976
p-CN-$C_6H_4NH_2$ – N from NH_2	-377.600286	-362.696351

Table S2. B3LYP total energy for initial and N(1s) ionized state of the molecules included in the validation set at the B3LYP optimized geometry.

	Total Energy (a.u.)	
Molecule	Initial State	Final State
NH_3	-56.551523	-41.656378
CH_3NH_2	-95.839434	-80.960885
$C_6H_5NH_2$	-287.540088	-272.655852
$C_6H_5NHCH_3$	-326.831682	-311.955678
$C_6H_5N(CH_3)_2$	-366.119876	-351.249310
C_6H_5CN	-324.421358	-309.553673
C_5H_5N	-248.228814	-233.367500
C_4H_4NH	-210.124951	-195.207493
HCN	-93.414394	-78.469900
CH_3CN	-132.732648	-117.837106
$(CH_3)_2NH$	-135.131782	-120.263263
$CH_3CH_2NH_2$	-135.143399	-120.272464
$(CH_3CH_2)_2NH$	-213.733822	-198.880144
$(CH_3)_3N$	-174.426170	-159.563170
$CH_3CH_2CH_2NH_2$	-174.443726	-159.575126
p-$(CH_3)_2NC_6H_4NH_2$ – N from $N(CH_3)_2$	-421.468054	-406.607434
p-$(CH_3)_2NC_6H_4NH_2$ – N from NH_2	-421.468054	-406.597263
p-CN-$C_6H_4NH_2$ – N from CN	-379.777470	-364.932595
p-CN-$C_6H_4NH_2$ – N from NH_2	-379.777470	-364.870906

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16. *CLIPS is a program system to compute ab initio SCF and correlated wavefunctions for polyatomic systems. It has been developed based on the publicly available programs in the ALCHEMY package from the IBM San Jose Research Laboratory by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine.*