Supporting Information

to

Unifying conceptual density functional and valence bond theory: The hardness-softness conundrum associated with protonation reactions and uncovering complementary reactivity modes

Thijs Stuyver,*[a] and Sason Shaik*[a]

[a.] Institute of Chemistry, Edmond J. Safara Campus at Givat Ram, The Hebrew University, Jerusalem 9190401, Israel

S1. Comparison of the BOVB results with the DFVB results for a selected subset of considered systems

From Table S1 it is clear that the bonding situations are equally well described by BOVB and DFVB level-of-theory; the only quantity that differs significantly between both methods is the bonding energy. The latter finding is in line with expectations, since DFVB generally does a better job at recovering the full bonding energy than BOVB (see also Section S2; cf. Ref. 46 in the main text).

Table S1. The weights of the HL and the main ionic structures (w_{HL} and $w_{ion,1}$), the resonance energy (RE) and the spacing between the HL and main ionic state ($\Delta E_{HL\text{-}ion,1}$) at the optimal bonding distance and the adiabatic bonding energy obtained for $[H_3N\text{-}H]^+$, $[H_2S\text{-}H]^+$ and $[H_2O\text{-}H]^+$ at respectively BOVB-d/6-311++G**//(U)B3LYP/def2-TZVP and DFVB(LYP)/6-311++G**//(U)B3LYP/def2-TZVP level-of-theory.

	w_{HL}	$w_{ion,1}$	RE[a]	$\Delta E_{HL\text{-}ion,1}$ [a]	Bonding energy[a]
$[H_3N\text{-}H]^+$ - BOVB	0.61	0.33	39.0	58.7	130.6
$[H_3N\text{-}H]^+$ - DFVB	0.62	0.36	34.8	56.3	138.6
$[H_2S\text{-}H]^+$ - BOVB	0.68	0.26	21.1	101.8	85.9
$[H_2S\text{-}H]^+$ - DFVB	0.68	0.26	21.7	98.7	95.4
$[H_2O\text{-}H]^+$ - BOVB	0.55	0.41	70.7	11.8	132.8
$[H_2O\text{-}H]^+$ - DFVB	0.56	0.44	63.8	9.3	146.8

[a] in kcal/mol

S2. Comparison of the DFVB results with the DFT results and experimental data

Table S2. The bonding energy and $A_H+ - I_R$ (in kcal/mol) computed at respectively DFVB(LYP)/6-311++G**//(U)B3LYP/def2-TZVP, (U)B3LYP/def2-TZVP(+ZPE) [DFT(a)], (U)B3LYP/6-311++G**//(U)B3LYP/def2-TZVP(+ZPE) [DFT(b)] level-of-theory and (experimental) literature values for $A_H+ - I_R$ for each of the systems considered in the main text. Note the significant overestimation of the $A_H+ - I_R$ value calculated with the DFVB method.

	Bonding energy DFVB	$A_H+ - I_R$ DFVB	Bonding energy DFT(a)	$A_H+ - I_R$ DFT(a)	Bonding energy DFT(b)	$A_H+ - I_R$ DFT(b)	$A_H+ - I_R$ literature
$[H_2S\text{-}H]^+$	95.4	83.9	95.1	73.6	93.7	73.1	72.5[1]
$[H_2O\text{-}H]^+$	146.8	39.3	143.2	21.0	143.9	19.7	22.6[1]
$[H_3N\text{-}H]^+$	138.6	80.0	140.0	62.7	140.6	62.7	66.8[2]
$[H_2NOH_2]^+$	97.6[a]	106.0[a]	98.3	70.1	98.5	68.7	/
$[H_3NOH]^+$	123.9[a]	106.0[a]	123.6	70.1	123.6	68.7	/
$[H_2NSH_2]^+$	98.5	106.0	93.3	90.8	100.7	77.9	/
$[H_3NSH]^+$	117.3	106.0	105.8	90.8	119.8	77.9	/
$[C_6H_5N\text{-}H]^+$	135.8[b]	120.6[b]	125.5	97.1	125.5	96.8	100.2[1]
$[C_6H_6N]^+_{ortho}$	71.2[b]	120.6[b]	69.5	97.1	70.4	96.8	100.2[1]

$[C_6H_6N]^+_{meta}$	82.5[b]	120.6[b]	76.2	97.1	77.0	96.8	100.2[1]
$[C_6H_6N]^+_{para}$	61.2[b]	120.6[b]	64.1	97.1	70.4	96.8	100.2[1]

[a] The geometry of dissociated H_3NOH was selected to evaluate the energetics in the asymptotic limit

[b] The geometry of dissociated N-protonated pyridine was selected to evaluate the energetics in the asymptotic limit

S3. Bond scanning profiles for the protonation reactions
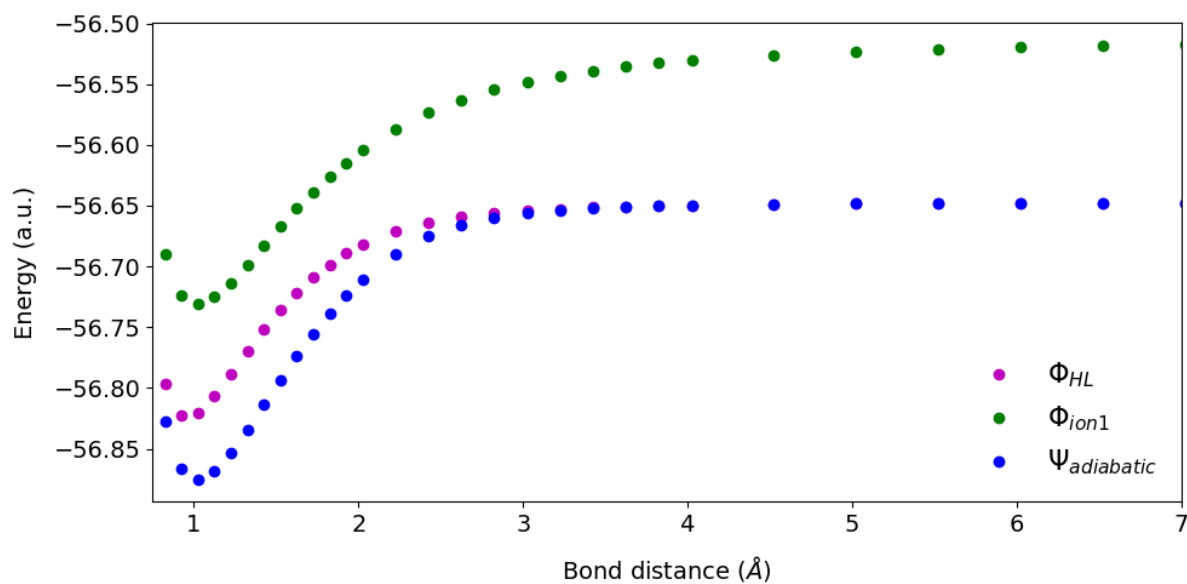
Figure S1. Evolution of the energy of Φ_{HL}, Φ_{ion1} and $\Psi_{adiabatic}$ as a function of the N-H bond distance in NH_4^+, calculated at DFVB(LYP)/6-311++G**//(U)B3LYP/def2-TZVP level-of-theory.
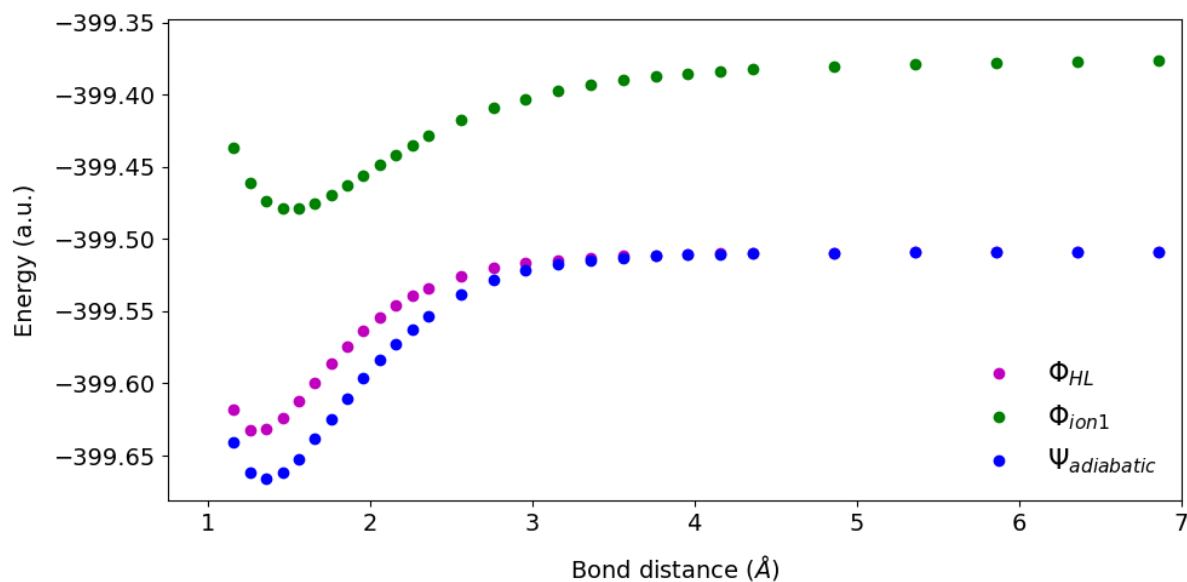
Figure S2. Evolution of the energy of Φ_{HL}, Φ_{ion1} and $\Psi_{adiabatic}$ as a function of the S-H bond distance in H_3S^+, calculated at DFVB(LYP)/6-311++G**//(U)B3LYP/def2-TZVP level-of-theory.
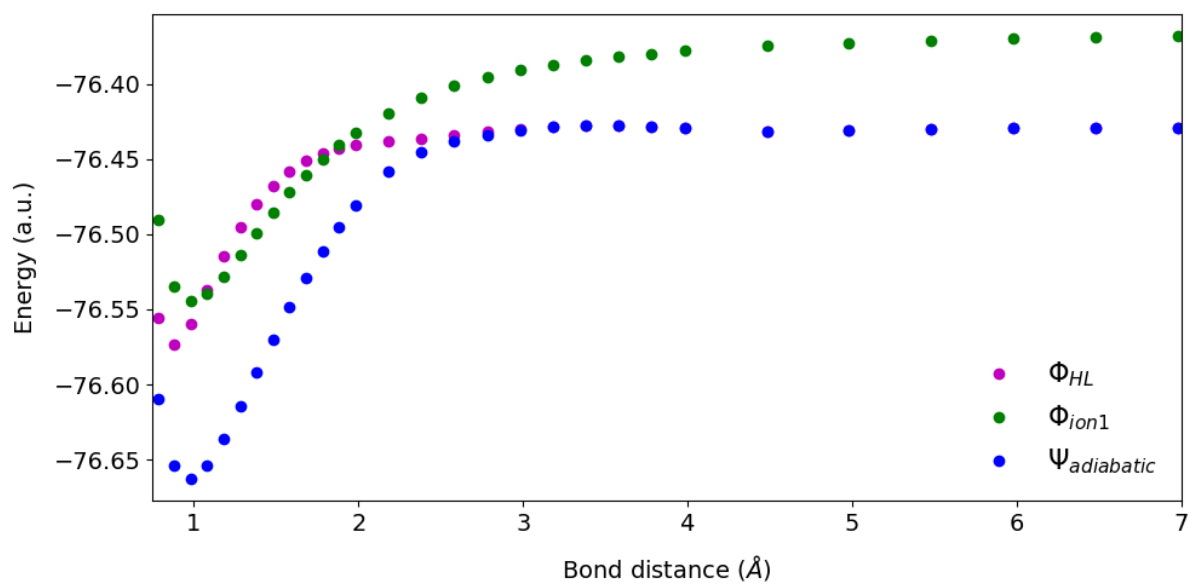
Figure S3. Evolution of the energy of Φ_{HL}, Φ_{ion1} and $\Psi_{adiabatic}$ as a function of the O-H bond distance in H_3O^+, calculated at DFVB(LYP)/6-311++G**//(U)B3LYP/def2-TZVP level-of-theory.

S4. Connection between the presented VB framework and the empirical factors previously identified as driving pKa values

In a set of recent papers, cf. Ref. 57 – 59 in the main text, Liu and co-workers connected a variety of electronic and reactivity descriptors emerging from a CDFT framework to the experimental acid strengths of a variety of structurally related sets of acidic compounds and complexes. Interestingly, the main factors probed/identified in these studies also emerge (in a modified version) in our own VB-based framework to describe protonation propensities:

    (a) The authors observed a (negatively sloped) linear correlation between the MEP value on the association site and the experimental pK_a values. As indicated in the main text, MEP values are good descriptors of the electrostatic part of the interaction energy. Hence, when a set of compounds with common structural features in close proximity of the protonation site (but varying substituents in more distant positions of the molecule or complex) are considered – resulting in a more or less constant spin-pairing/ (frontier) orbital contribution across the series but a variable electrostatic (long-range) contribution – then this descriptor can be expected to correlate well with the experimental pK_a values.

    (b) The authors observed a (positively sloped) linear correlation between the chemical potential of the reaction partner R ($\mu_R = \frac{1}{2}[I_R + A_R]$) and the experimental pK_a values. This finding can also be connected to our model through realization that μ_R acts as a probe for the spacing between the HL and ionic structure in our model, i.e. $I_H - I_R$ (cf. Eq. 2 in the main text): since A_R is a rather small quantity in most (saturated) organic compounds (relative to I_R) and I_H is by definition a constant for all protonation processes, the magnitude of μ_R effectively acts as an indicator of the magnitude of I_R. Hence, this quantity tells us something about the magnitude of the

spin-pairing interaction when a single elemental type is considered for the association site within a set of structurally related acids. This realization is further corroborated by the finding in other studies that the pK_a correlates with $E_{HOMO,R}$ (another quantity connected to I_R), cf. Ref. 65.

S5. Comparison between the VB-analogue of the Fukui function and the conventional Fukui function

Throughout the main text, we focus on the VB-inspired analogue of the Fukui function, i.e. the spin density of the (positively) charged compound, as a descriptor of the spin-pairing/orbital interaction. In the literature, this descriptor is often referred to as a so-called "Parr function". As indicated in Ref. 61 and 62 in the main text, this descriptor corresponds – within reasonable bounds – to the traditional (CDFT) definition of the Fukui function (in its finite difference approximation), i.e. $f^-(\underline{r}) = \rho_N(\underline{r}) - \rho_{N-1}(\underline{r})$. Below, this finding was verified for each of the systems considered in the present study. Note that while there are numerical shifts between the two spin-pairing/orbital interaction descriptors, the emerging trends are identical.

Table S3. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for NH_3, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
N	0.81261	1.04088
H	0.06246	-0.01363
H	0.06246	-0.01363
H	0.06246	-0.01363

Table S4. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for H_2S, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
S	0.92495	1.04124
H	0.03752	-0.02062
H	0.03752	-0.02062

Table S5. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for H_2O, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
O	0.86881	1.04218
H	0.06559	-0.0211
H	0.06559	-0.02109

Table S6. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for H_2NOH, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
N	0.54246	0.80068
H	0.08287	-0.00691
H	0.08287	-0.00691
O	0.21194	0.1971
H	0.07987	0.01605

Table S7. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for H_2NSH, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
N	0.00073	-0.01005
H	0.06973	0.02049
H	0.06976	0.02051
S	0.82356	0.98757
H	0.03622	-0.01852

Table S8. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for HONHOH, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
N	0.37779	0.59123
H	0.08587	-0.00746
O	0.2049	0.20265
H	0.06327	0.00547
O	0.20491	0.20266
H	0.06327	0.00546

Table S9. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for HSNHSH, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
N	-0.03732	-0.01738
H	0.03542	-0.0018

S	0.46203	0.51894
H	0.03894	-0.00933
S	0.462	0.51891
H	0.03893	-0.00933

Table S10. Comparison between the atom-condensed conventional Fukui function and its VB-inspired analogue for pyridine, derived from the ground-state wavefunctions calculated at (U)B3LYP/def2-TZVP level-of-theory.

	Conventional Fukui function (in au)	VB-inspired analogue of the Fukui function (in au)
C_{ortho}	-0.02148	-0.01812
C_{meta}	0.06172	0.078
C_{para}	0.08453	-0.02916
C_{meta}	0.06172	0.078
C_{ortho}	-0.02148	-0.01812
N	0.4744	0.82536
H	0.05843	0.01419
H	0.08826	0.02756

H	0.06283	0.00737
H	0.06283	0.00737
H	0.08825	0.02756

S6. Spin densities of the ground-state and first excited state for [HSHNSH]$^{+\bullet}$ in its optimal and twisted geometry

Ground state HSNHSH_opt
$\rho(S) = 0.52$; $\rho(N) = -0.02$

First excited state HSNHSH_opt
$\rho(S) = 0.16$; $\rho(N) = 0.53$

Ground state HSNHSH_twisted
$\rho(S\_left) = 0.56$; $\rho(N) = 0.37$; $\rho(S\_right) = 0.03$

First excited state HSNHSH_twisted
$\rho(S\_left) = 0.24$; $\rho(N) = 0.03$; $\rho(S\_right) = 0.73$
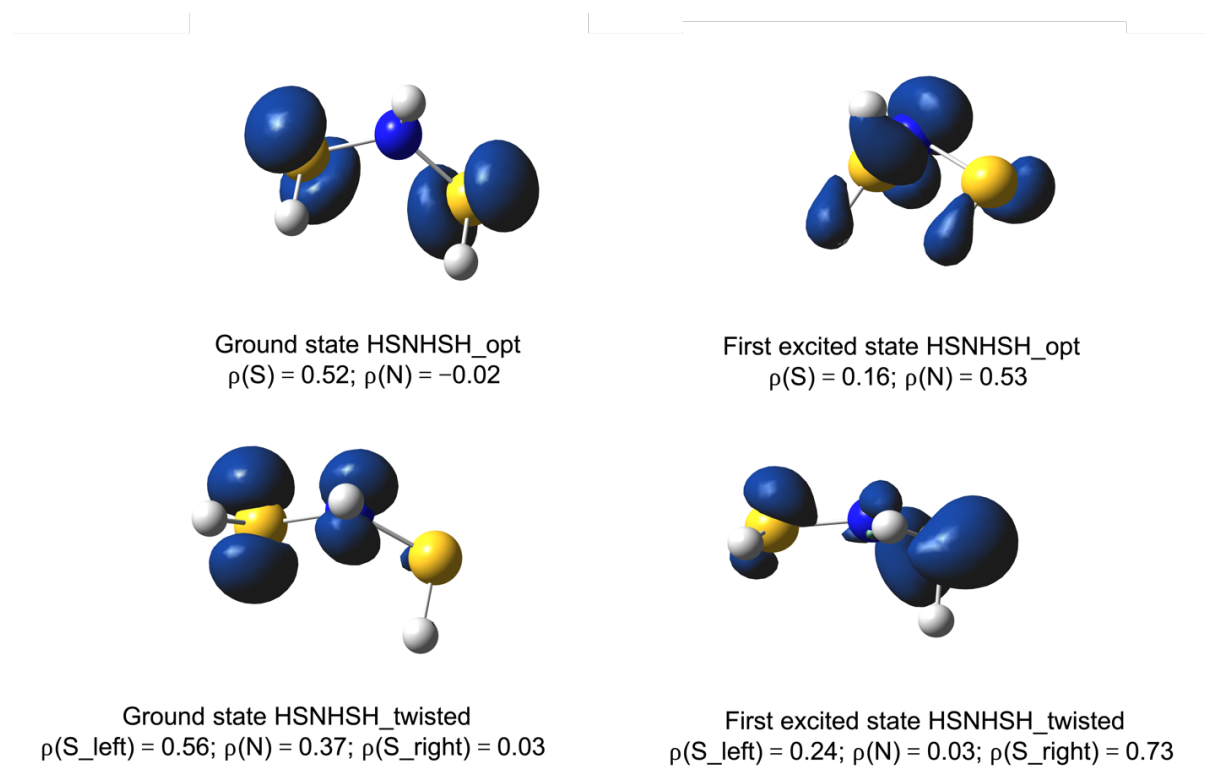
Figure S4. The spin density associated with the ground-state and first excited state of [HSHNSH]$^{+\bullet}$ in its optimal geometry ($\Delta E_{excitation} = 11.7$ kcal/mol) and the geometry in which the dihedral angle H-S-N-H has been twisted to maximize the overlap between the lone pairs ($\Delta E_{excitation} = 22.5$ kcal/mol).

S7. Tuning the state ordering through captodative substitution

a)

Ground state   First excited state

b)

Ground state   First excited state
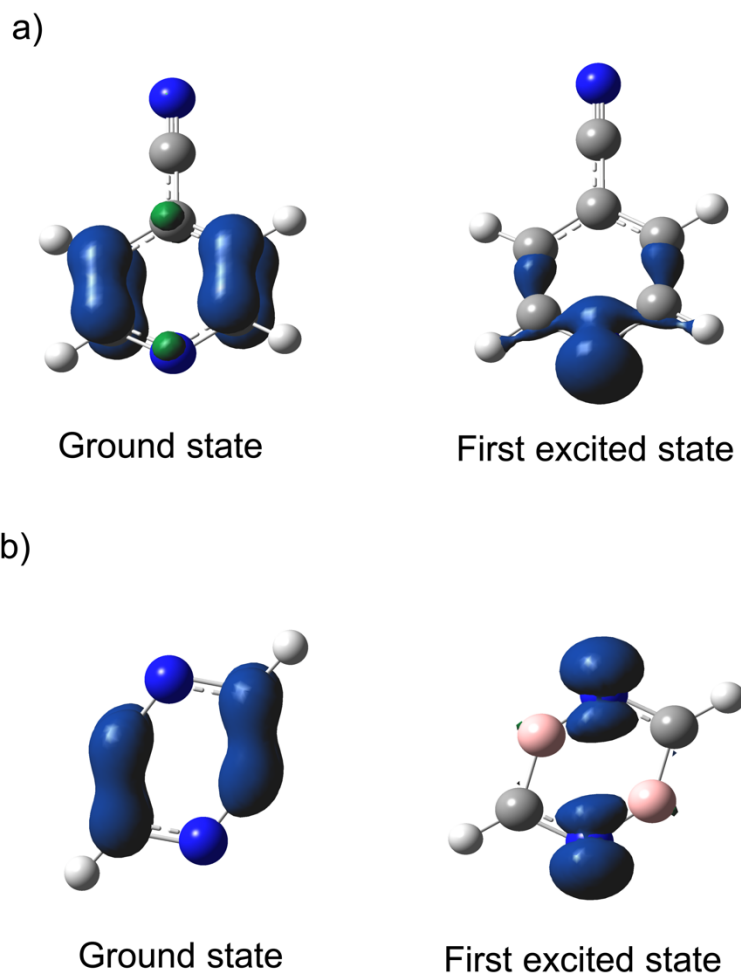
Figure S5. a) Spin density contour maps for the ground- and first excited state of [4-cyano pyridine]$^{+\bullet}$; b) spin density maps for the ground- and first excited state of [C$_2$B$_2$N$_2$H$_4$]$^{+\bullet}$.

S8. Utility to scan for a minimum electrostatic potential value

As indicated in the main text, a small utility was written to scan for the minimum value of the electrostatic potential along a specific axis away from the atom center for pyridine. The utility takes a regular Gaussian .cube file as input. Because the pyridine molecule in our calculation was aligned with the xy-plane, the electrostatic potential for the C-sites could simply be scanned in the z-direction; the electrostatic potential for the in-plane lone pair associated with the N-site was scanned in the y-direction.

For the ortho-site, the minimum of the electrostatic potential (reached at a distance of 2.3 Å from the atomic center) amounted to -6.7 kcal/mol. For the meta-site, this quantity amounted to -5.1 kcal/mol and for the para-site to -3.9 kcal/mol (reached at 2.2 Å and 2.1 Å respectively). For the N-site, the minimum, amounting to -59.0 kcal/mol, was reached at a distance of 1.4 Å away from the atom center.

The full code is displayed below.

```python
import math

def read_cube_file(filename, N1, N2, N3):
    """ reads in the .cube file into a 3D-matrix object by iterating
through the N1, N2 and N3 dimensions """
    matrix = []

    with open(filename, 'r') as f_obj:
        contents = f_obj.read()
        line_list = contents.split("\n")
        f_obj.close()

    for i in range(N1):
        matrix.append([])
        for j in range(N2):
            matrix[i].append([])

    full_value_list = []

    for line in line_list:
        temp_list = list(map(float, tuple(line.split())))

        for number in temp_list:
            full_value_list.append(number)
```

```python
    for i in range(N1):
        for j in range(N2):
            for k in range(N3):
                matrix[i][j].append(full_value_list[i * N2 * N3 + j * N3 +
k])

    return matrix

def convert_point_to_matrix_element(pointx, pointy, pointz, incrementx,
incrementy, incrementz, startx, starty, startz):
    """ Converts (pointx, pointy, pointz) into the corresponding matrix
element in the 3D-matrix """
    i = (pointx - startx)/incrementx
    j = (pointy - starty) / incrementy
    k = (pointz - startz) / incrementz

    return int(i), int(j), int(k)

def determine_minimum_in_direction(matrix, x, y, z, dir):
    """ Scans the 3D-matrix from (x, y, z) along dir to find the minimum
value """
    minimum = matrix[x][y][z]
    if dir == "z":
        for i in range(30):
            if minimum > matrix[x][y][z+i]:
                minimum = matrix[x][y][z+i]
                a, b, c = x, y, z+i
    elif dir == "y":
        for i in range(20):
            if minimum > matrix[x][y+i][z]:
                minimum = matrix[x][y+i][z]
                a, b, c = x, y+i, z

    return a, b, c, minimum

def determine_distance(i, j, k, a, b, c, incrementx, incrementy,
incrementz):
    """ Determines the distance between the atom center and the point at
which the minimum
    in the electrostatic potential is found """
    distance = math.sqrt(((i-a) * incrementx)**2 + ((j-b) * incrementy)**2
+ ((k-c) * incrementz)**2)
    return distance

#_____

matrix = read_cube_file("pyridine_potential.cube", 89, 87, 66)

#ortho
i, j, k = convert_point_to_matrix_element(-
2.152577,1.359378,0.000186,0.200015,0.200015,0.200015,-8.767684,-9.118581,-
6.513126)
a, b, c, minimum = determine_minimum_in_direction(matrix, i, j, k, "z")
distance = determine_distance(i, j, k, a, b, c, 0.200015,0.200015,0.200015)
print("Minimum electrostatic potential for the ortho-position: ", minimum,
" au, reached at a distance of ", distance)

#meta
i, j, k = convert_point_to_matrix_element(-2.254932, -1.265736,
0.000396,0.200015,0.200015,0.200015,-8.767684,-9.118581,-6.513126)
```

```
a, b, c, minimum = determine_minimum_in_direction(matrix, i, j, k, "z")
distance = determine_distance(i, j, k, a, b, c, 0.200015,0.200015,0.200015)
print("Minimum electrostatic potential for the meta-position: ", minimum, "
au, reached at a distance of ", distance)

#para
i, j, k = convert_point_to_matrix_element(0.000054,-
2.605829,0.000171,0.200015,0.200015,0.200015,-8.767684,-9.118581,-6.513126)
a, b, c, minimum = determine_minimum_in_direction(matrix, i, j, k, "z")
distance = determine_distance(i, j, k, a, b, c, 0.200015,0.200015,0.200015)
print("Minimum electrostatic potential for the para-position: ", minimum, "
au, reached at a distance of ", distance)

#N-site
i, j, k = convert_point_to_matrix_element(-0.000055,2.669695,-
0.000173,0.200015,0.200015,0.200015,-8.767684,-9.118581,-6.513126)
a, b, c, minimum = determine_minimum_in_direction(matrix, i, j, k, "y")
distance = determine_distance(i, j, k, a, b, c, 0.200015,0.200015,0.200015)
print("Minimum electrostatic potential for the N-position: ", minimum, "
au, reached at a distance of ", distance)
```

S9. Geometries and Energies

Units:

- Coordinates are expressed in Å

- Energies are expressed in a.u.

H₂

H	-0.481363	-3.249661	0.000000
H	-1.225286	-3.249661	0.000000

(U)B3LYP/def2-TZVP energy = -1.1796489903919316

NaCl

Na	-2.129712	1.037992	0.000000
Cl	-4.493666	1.037992	0.000000

(U)B3LYP/def2-TZVP energy = -622.6050541289729

NH3

N	-0.871712	2.101449	0.000000
H	-0.500437	1.158565	-0.000300
H	-0.500420	2.572625	0.816708
H	-0.500420	2.573144	-0.816408

(U)B3LYP/def2-TZVP energy = -56.585678339117926

[NH₄]⁺

N	-0.924598	2.092591	0.040711
H	-0.570376	1.130921	0.018242
H	-0.536419	2.580887	0.854135
H	-0.644267	2.580092	-0.816353
H	-1.947467	2.078469	0.106738

(U)B3LYP/def2-TZVP energy = -56.92385303636355

H₂O

O	-0.670391	2.177221	0.000000
H	0.291742	2.212724	0.000000
H	-0.958092	3.096019	0.000000

(U)B3LYP/def2-TZVP energy = -76.4629947772201

[H₃O]⁺

O	-0.715808	2.159692	0.075634
H	0.252145	2.085289	-0.066701
H	-1.059719	3.070170	-0.048750
H	-1.234117	1.477966	-0.403304

(U)B3LYP/def2-TZVP energy = -76.7375601749838

H₂S

S	-0.725065	2.099859	0.000000
H	0.602802	2.298244	0.000000
H	-0.981309	3.417784	0.000000

(U)B3LYP/def2-TZVP energy = -399.425346346739

[H₃S]

H	-1.280270	1.422995	-0.555014
S	-0.698741	2.173308	0.415581
H	0.525855	2.168726	-0.170555
H	-1.071175	3.358010	-0.133135

(U)B3LYP/def2-TZVP energy = -399.7048610444624

H₂NOH

N	-1.425905	0.298973	0.018383
H	-1.005564	-0.626852	-0.003445
H	-1.005663	0.780854	0.809270
O	-0.867789	0.964426	-1.134239
H	-1.653340	1.243215	-1.617321

(U)B3LYP/def2-TZVP energy = -131.7778760266885

[H₂NOH₂]⁺

N	-1.404324	0.350623	0.121598
H	-1.268622	-0.646370	-0.053016
H	-0.821605	0.652010	0.904759
O	-0.794855	0.959242	-1.082970
H	0.160783	1.179337	-1.047443
H	-1.347441	1.719700	-1.357735

(U)B3LYP/def2-TZVP energy = -132.058357824404

[H₃NOH]⁺

O	-0.958294	1.263720	-1.031207
H	-1.361592	0.985847	-1.874734
N	-1.410813	0.383461	-0.037046
H	-1.110965	-0.585680	-0.212278
H	-0.964973	0.712276	0.828224
H	-2.432259	0.427503	0.083554

(U)B3LYP/def2-TZVP energy = -132.10069622405916

H$_2$NSH

N	-1.341546	0.336401	-0.046362
H	-1.059740	-0.634287	-0.021917
H	-1.059694	0.800500	0.806526
S	-0.684085	1.130825	-1.422479
H	-1.851968	1.467387	-2.005207

(U)B3LYP/def2-TZVP energy = -454.7852277958409

[H$_3$NSH]$^+$

H	-1.379070	0.966023	-2.128576
N	-1.390287	0.326412	0.102637
H	-1.244690	-0.661754	-0.123912
H	-0.943065	0.509403	1.006702
H	-2.392324	0.511216	0.206383
S	-0.617351	1.425820	-1.116049

(U)B3LYP/def2-TZVP energy = -455.11232949317673

[H$_2$NSH$_2$]$^+$

N	-1.221359	0.256065	0.119855
H	-1.423849	-0.734457	0.114531
H	-0.939228	0.672977	0.996751
S	-0.809981	0.892049	-1.309651
H	0.480498	1.314139	-1.194546
H	-1.328975	2.143696	-1.241748

(U)B3LYP/def2-TZVP energy = -455.0888253933681

C$_5$H$_5$N

C	-3.974867	-1.498504	0.000012
C	-2.584665	-1.502016	-0.000065
C	-1.919469	-0.283680	-0.000276
C	-2.671675	0.882943	-0.000395
C	-4.057925	0.778139	-0.000284
N	-4.709300	-0.385463	-0.000094
H	-0.837377	-0.244211	-0.000353

H	-4.525251	-2.433730	0.000180
H	-2.041940	-2.438254	0.000038
H	-2.198629	1.856247	-0.000567
H	-4.674998	1.670770	-0.000387

(U)B3LYP/def2-TZVP energy = -248.3789997769894

[C₅H₅N-H]⁺

C	-1.184942	-0.676531	0.128909
C	-1.206177	0.695067	0.006561
C	0.000255	1.387464	-0.055018
C	1.206422	0.694635	0.006894
C	1.184663	-0.676954	0.129236
H	0.000461	2.465345	-0.151202
H	-2.071880	-1.290851	0.183730
H	-2.154870	1.209997	-0.039544
H	2.155312	1.209227	-0.038948
H	2.071367	-1.291591	0.184303
N	-0.000261	-1.314634	0.185987
H	-0.000454	-2.324938	0.275543

(U)B3LYP/def2-TZVP energy = -248.74802257398377

[C₅H₆N]⁺ₒᵣₜₕₒ

C	-0.58305500	1.24064000	-0.00010700
C	0.79506200	1.19857800	0.00000100
C	1.38927500	-0.05577100	0.00007900
C	0.60233600	-1.25564100	-0.00005900
N	-0.68989500	-1.24698800	-0.00006000
H	1.39188000	2.10079000	-0.00000600
H	-1.12036100	2.18312500	-0.00023400
H	2.47029900	-0.14505600	0.00012100
H	1.10231400	-2.21892900	-0.00013700
C	-1.34781900	0.00385900	0.00003900
H	-2.07530000	0.00945100	-0.83814000
H	-2.07436900	0.00953600	0.83909500

(U)B3LYP/def2-TZVP energy = -248.6537621

[C₅H₆N]⁺ₚₐᵣₐ

C	-1.171007	-0.743170	-0.000215
C	-1.237101	0.632895	-0.000136
C	1.237334	0.632449	0.000206
C	1.170743	-0.743593	0.000110
N	-0.000250	-1.397709	-0.000094
H	-2.063743	-1.356323	-0.000376
H	-2.188234	1.151348	-0.000234

H	2.188654	1.150559	0.000371
H	2.063258	-1.357067	0.000193
C	0.000254	1.398478	0.000086
H	0.000269	2.123196	0.841081
H	0.000501	2.123321	-0.840800

(U)B3LYP/def2-TZVP energy = -248.6441624748297

$[C_5H_6N]^+_{meta}$

C	-1.144165	-0.716737	-0.000212
C	-1.225547	0.688811	-0.000131
C	-0.062006	1.398597	0.000084
C	1.120390	-0.781278	0.000102
N	-0.002933	-1.441143	-0.000101
H	-0.057892	2.482277	0.000160
H	-2.057259	-1.304723	-0.000370
H	-2.193683	1.170537	-0.000236
H	2.038154	-1.364318	0.000186
C	1.216755	0.684547	0.000216
H	1.846864	1.009037	-0.849300
H	1.846629	1.008926	0.849948

(U)B3LYP/def2-TZVP energy = -248.6639278746687