Supporting Information

to

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

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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 (\(\Delta E_{HL-ion,1}\)) at the optimal bonding distance and the adiabatic bonding energy obtained for [H$_3$N-H]$^+$, [H$_2$S-H]$^+$ and [H$_2$O-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 \(^a\) | \(\Delta E_{HL-ion,1}\) \(^a\) | Bonding energy \(^a\) |
|------------------|-------------|---------------|-----------|-------------------------------|----------------------|
| [H$_3$N-H]$^+$ - BOVB | 0.61        | 0.33          | 39.0      | 58.7                          | 130.6                |
| [H$_3$N-H]$^+$ - DFVB | 0.62        | 0.36          | 34.8      | 56.3                          | 138.6                |
| [H$_2$S-H]$^+$ - BOVB | 0.68        | 0.26          | 21.1      | 101.8                         | 85.9                 |
| [H$_2$S-H]$^+$ - DFVB | 0.68        | 0.26          | 21.7      | 98.7                          | 95.4                 |
| [H$_2$O-H]$^+$ - BOVB | 0.55        | 0.41          | 70.7      | 11.8                          | 132.8                |
| [H$_2$O-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 | $A_{H^+} - I_R$ | Bonding energy | $A_{H^+} - I_R$ | Bonding energy | $A_{H^+} - I_R$ | Bonding energy | $A_{H^+} - I_R$ | $A_{H^+} - I_R$ |
|----------|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|
|          | DFVB           | DFVB            | DFT(a)         | DFT(a)          | DFT(b)         | DFT(b)          | DFT(b)         | DFT(b)          | literature     |
| [H$_2$S-H]$^+$ | 95.4           | 83.9            | 95.1           | 73.6            | 93.7           | 73.1            | 72.5$^1$       |
| [H$_2$O-H]$^+$ | 146.8          | 39.3            | 143.2          | 21.0            | 143.9          | 19.7            | 22.6$^1$       |
| [H$_3$N-H]$^+$ | 138.6          | 80.0            | 140.0          | 62.7            | 140.6          | 62.7            | 66.8$^2$       |
| [H$_2$NOH$_2$]$^+$ | 97.6$^a$       | 106.0$^a$       | 98.3           | 70.1            | 98.5           | 68.7            | /              |
| [H$_3$NOH]$^+$ | 123.9$^a$      | 106.0$^a$       | 123.6          | 70.1            | 123.6          | 68.7            | /              |
| [H$_2$NSH$_2$]$^+$ | 98.5           | 106.0           | 93.3           | 90.8            | 100.7          | 77.9            | /              |
| [H$_3$NSH]$^+$ | 117.3          | 106.0           | 105.8          | 90.8            | 119.8          | 77.9            | /              |
| [C$_6$H$_5$N-H]$^+$ | 135.8$^b$     | 120.6$^b$       | 125.5          | 97.1            | 125.5          | 96.8            | 100.2$^1$      |
| [C$_6$H$_6$N]$^+$$_{ortho}$ | 71.2$^b$       | 120.6$^b$       | 69.5           | 97.1            | 70.4           | 96.8            | 100.2$^1$      |

S3
\[
\begin{array}{cccccc}
[C_6H_5N]^+_{\text{meta}} & 82.5^b & 120.6^b & 76.2 & 97.1 & 77.0 & 96.8 & 100.2^l \\
[C_6H_5N]^+_{\text{para}} & 61.2^b & 120.6^b & 64.1 & 97.1 & 70.4 & 96.8 & 100.2^l \\
\end{array}
\]

\(^a\) The geometry of dissociated H\textsubscript{3}NOH 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 $\Phi_{HL}$, $\Phi_{ion1}$ 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 $\Phi_{HL}$, $\Phi_{ion1}$ and $\Psi_{adiabatic}$ as a function of the S-H bond distance in H$_3$S$,^+$, calculated at DFVB(LYP)/6-311++G**(U)B3LYP/def2-TZVP level-of-theory.
Figure S3. Evolution of the energy of $\Phi_{\text{HL}}$, $\Phi_{\text{ion1}}$ and $\Psi_{\text{adiabatic}}$ as a function of the O-H bond distance in H$_3$O$^+$, 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 pKₐ 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 pKₐ 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 pKₐ values. This finding can also be connected to our model through realization that \( \mu_R \) 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 \( \mu_R \) 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 pKₐ 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. \( f^-(\mathbf{r}) = \rho_{N}(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \). 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$_2$S, 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$_2$O, 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$_2$NOH, 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$_2$NSH, 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                                          |
|   | Conventional Fukui function (in au) | VB-inspired analogue of the Fukui function (in au) |
|---|-------------------------------------|-----------------------------------------------|
| C<sub>ortho</sub> | -0.02148 | -0.01812 |
| C<sub>meta</sub> | 0.06172 | 0.078 |
| C<sub>para</sub> | 0.08453 | -0.02916 |
| C<sub>meta</sub> | 0.06172 | 0.078 |
| C<sub>ortho</sub> | -0.02148 | -0.01812 |
| N | 0.4744 | 0.82536 |
| H | 0.05843 | 0.01419 |
| H | 0.08826 | 0.02756 |

**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.
| 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]^• in its optimal and twisted geometry

**Figure S4.** The spin density associated with the ground-state and first excited state of [HSHNSH]^• in its optimal geometry ($\Delta E_{\text{excitation}} = 11.7$ 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 ($\Delta E_{\text{excitation}} = 22.5$ kcal/mol).
S7. Tuning the state ordering through captodative substitution

Figure S5. a) Spin density contour maps for the ground- and first excited state of [4-cyano pyridine]$^{••}$; b) spin density maps for the ground- and first excited state of [C$_2$B$_2$N$_2$H$_4$]$^{••}$. 
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)
```
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, incremeny, incrementz, startx, stary, startz):
    """ Converts (pointx, pointy, pointz) into the corresponding matrix element in the 3D-matrix """
    i = (pointx - startx)/incrementx
    j = (pointy - stary) / 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, incremeny, 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) * incremeny)**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, -2.655829, 0.000171, 0.200015, 0.200015, -8.7667684, -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**

|   | α    | β     |          |
|---|------|-------|----------|
| H | -0.481363 | -3.249661 | 0.000000 |
| H | -1.225286  | -3.249661 | 0.000000 |

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

**NaCl**

|   | α    | β     |          |
|---|------|-------|----------|
| Na| -2.129712 | 1.037992 | 0.000000 |
| Cl| -4.493666 | 1.037992 | 0.000000 |

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

**NH₃**

|   | α    | β     |          |
|---|------|-------|----------|
| 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]⁺**

|   | α    | β     |          |
|---|------|-------|----------|
| 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**

|   | α    | β     |          |
|---|------|-------|----------|
| 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
|                 | X     | Y     | Z     |
|----------------|-------|-------|-------|
| **[H₂O]⁺**     |       |       |       |
| 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 |

| **[H₂S]**      |       |       |       |
| 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

**CsH$_5$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 |
\begin{align*}
\text{H} & \quad -4.525251 \quad -2.433730 \quad 0.000180 \\
\text{H} & \quad -2.041940 \quad -2.438254 \quad 0.000038 \\
\text{H} & \quad -2.198629 \quad 1.856247 \quad -0.000567 \\
\text{H} & \quad -4.674998 \quad 1.670770 \quad -0.000387 \\
\end{align*}

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

\begin{align*}
\text{[CsH}_5\text{N-H]}^+ & \\
\text{C} & \quad -1.184942 \quad -0.676531 \quad 0.128909 \\
\text{C} & \quad -1.206177 \quad 0.695067 \quad 0.006561 \\
\text{C} & \quad 0.000255 \quad 1.387464 \quad -0.055018 \\
\text{C} & \quad 1.206422 \quad 0.694635 \quad 0.006894 \\
\text{C} & \quad 1.184663 \quad -0.679545 \quad 0.129236 \\
\text{H} & \quad 0.000461 \quad 2.465345 \quad -0.151202 \\
\text{H} & \quad -2.071880 \quad -1.290851 \quad 0.183730 \\
\text{H} & \quad -2.154870 \quad 1.209997 \quad -0.039544 \\
\text{H} & \quad 2.155312 \quad 1.209227 \quad -0.038948 \\
\text{H} & \quad 2.071367 \quad -1.291591 \quad 0.184303 \\
\text{N} & \quad -0.000261 \quad -1.314634 \quad 0.185987 \\
\text{H} & \quad -0.000454 \quad -2.324938 \quad 0.275543 \\
\end{align*}

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

\begin{align*}
\text{[CsH}_6\text{N]}^+_{\text{ortho}} & \\
\text{C} & \quad -0.5830550 \quad 1.2406400 \quad -0.0001070 \\
\text{C} & \quad 0.7950620 \quad 1.1985780 \quad 0.0000010 \\
\text{C} & \quad 1.3892750 \quad -0.0557710 \quad 0.0007900 \\
\text{C} & \quad 0.6023360 \quad -1.2556410 \quad -0.0000590 \\
\text{N} & \quad -0.6899950 \quad -1.2469880 \quad -0.0000600 \\
\text{H} & \quad 1.3918800 \quad 2.1007900 \quad -0.0000060 \\
\text{H} & \quad -1.1203610 \quad 2.1831250 \quad -0.0002340 \\
\text{H} & \quad 2.4702990 \quad -0.1450560 \quad 0.0001210 \\
\text{H} & \quad 1.1023140 \quad -2.2189290 \quad -0.0001370 \\
\text{C} & \quad -1.3478190 \quad 0.0038590 \quad 0.0000390 \\
\text{H} & \quad -2.0753000 \quad 0.0094510 \quad -0.8381400 \\
\text{H} & \quad -2.0743690 \quad 0.0095360 \quad 0.8390950 \\
\end{align*}

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

\begin{align*}
\text{[CsH}_6\text{N]}^+_{\text{para}} & \\
\text{C} & \quad -1.171007 \quad -0.743170 \quad -0.000215 \\
\text{C} & \quad -1.237101 \quad 0.632895 \quad -0.000136 \\
\text{C} & \quad 1.237334 \quad 0.632449 \quad 0.000206 \\
\text{C} & \quad 1.170743 \quad -0.743593 \quad 0.000110 \\
\text{N} & \quad -0.000250 \quad -1.397709 \quad -0.000094 \\
\text{H} & \quad -2.063743 \quad -1.356323 \quad -0.000376 \\
\text{H} & \quad -2.188234 \quad 1.151348 \quad -0.000234 \\
\end{align*}
| Atom | U_B3LYP/def2-TZVP Energy | Meta Energy |
|------|--------------------------|-------------|
| C    | -1.144165                | -248.644162 |
| C    | -1.225547                | -248.663927 |
| C    | -0.062006                |             |
| C    | 1.120390                 |             |
| N    | -0.002933                |             |
| H    | -0.057892                |             |
| H    | -2.057259                |             |
| H    | -2.193683                |             |
| H    | 2.038154                 |             |
| C    | 1.216755                 |             |
| H    | 1.846864                 |             |
| H    | 1.846629                 |             |

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

| C5H6N + | U_B3LYP/def2-TZVP Energy | Meta Energy |
|---------|--------------------------|-------------|
| C       | -0.716737                | -248.663927 |
| C       | 0.688811                 |             |
| C       | 1.398597                 |             |
| C       | -0.781278                |             |
| N       | -1.441143                |             |
| H       | 2.482277                 |             |
| H       | -1.304723                |             |
| H       | 1.170537                 |             |
| H       | -1.364318                |             |
| C       | 0.684547                 |             |
| H       | 1.009037                 |             |
| H       | 1.008926                 |             |

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