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# Supporting Information for:

# A Practical Computational Approach to Study Molecular Instability Using the Pseudo Jahn-Teller Effect

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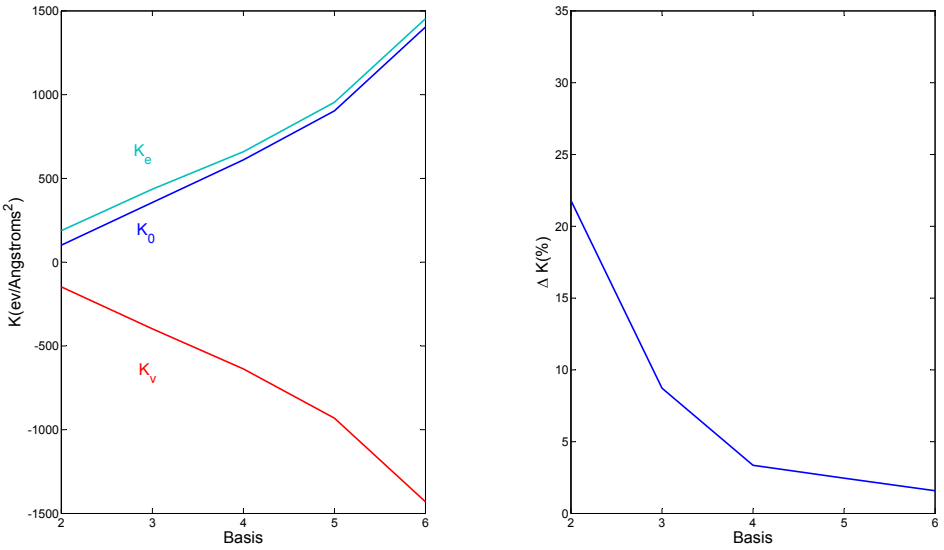


Figure S1: Calculation of the total contributions to the force constant at LDA level, (left) $K_0$ (blue), $K_v$ (red) and $K_e$ (green) varying the basis quality along the series cc-pvXz (X=d, t, q, 5, 6) in $NH_3$; (right) Comparison of the absolute value of $K_v$ and $K_e$, $\Delta K = |Kv/Ke| - 1$ in % varying the basis quality

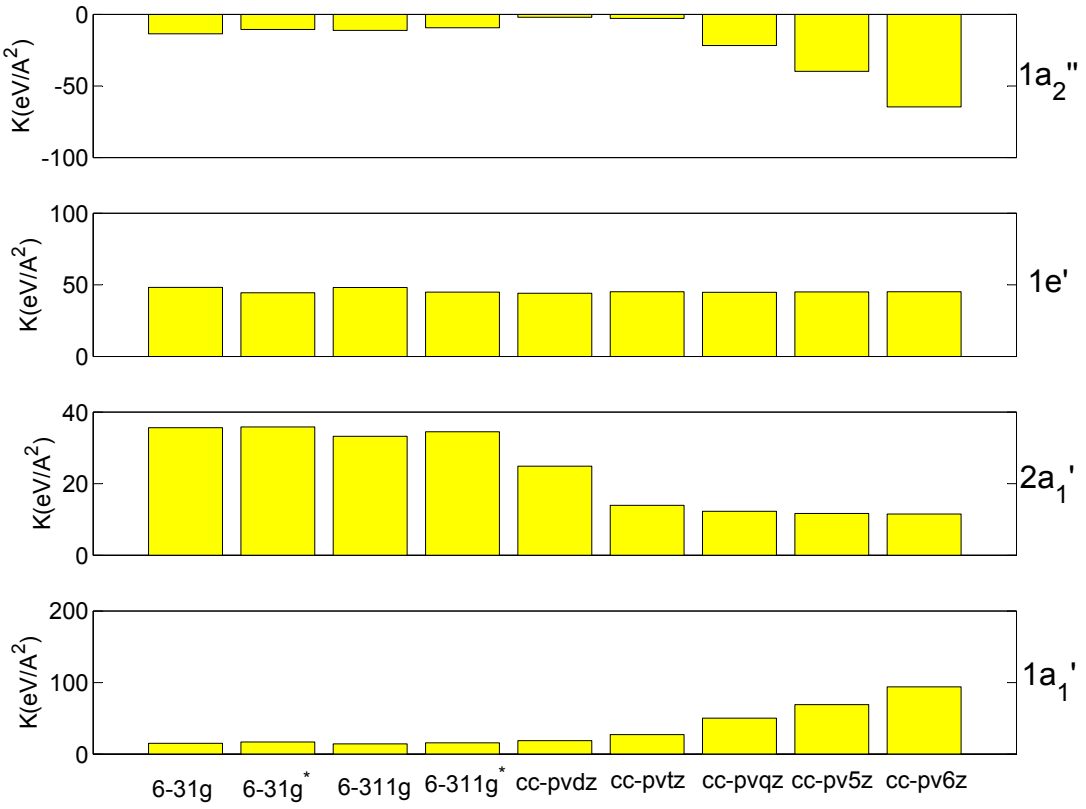


Figure S2: Calculation of the orbital contributions for each of the occupied orbitals of $NH_3$ to the total force constant for several basis-sets at LDA level of theory

Table S1: Orbital contributions for $NH_3$ and $BH_3$ at GGA (BLYP and PBE)/cc-pvtz level of theory. The orbital contributions are given per individual orbital, i.e. the $e'$ orbital total contribution is twice the one in the table due to the degeneracy. Units are eV/Å$^2$.

| | | BLYP | | | | PBE | | | |
|---|---|---|---|---|---|---|---|---|---|
| System | Contribution | $K_0$ | $2K_v$ | $K_e$ | K | $K_0$ | $2K_v$ | $K_e$ | $K$ |
| $NH_3$ | $1a'_1$ | 58.84 | -64.14 | 39.91 | 34.61 | 48.24 | -64.02 | 39.97 | 24.18 |
| | $2a'_1$ | 84.35 | -110.52 | 40.69 | 14.53 | 80.13 | -110.09 | 43.58 | 13.62 |
| | $1e'$ | 107.29 | -153.53 | 90.17 | 43.93 | 103.76 | -152.93 | 94.85 | 45.68 |
| | $1a''_2$ | 171.84 | -322.55 | 147.23 | -3.49 | 168.69 | -324.09 | 153.58 | -1.83 |
| | Nuclear | -150.88 | 0.0 | 0.0 | -150.88 | 150.88 | 0.0 | 0.0 | -150.88 |
| | DFT XC | 0.0 | 0.0 | 14.07 | 14.07 | 0.0 | 0.0 | 20.18 | 20.18 |
| | Total | 378.74 | -804.28 | 422.24 | -3.30 | 353.70 | -804.07 | 447.01 | -3.37 |
| $BH_3$ | $1a'_1$ | 26.87 | -24.16 | 12.18 | 14.89 | 24.77 | -24.17 | 12.14 | 12.74 |
| | $2a'_1$ | 30.11 | -28.70 | 8.22 | 9.62 | 29.12 | -28.35 | 8.80 | 9.56 |
| | $1e'$ | 55.49 | -73.29 | 20.77 | 20.77 | 54.24 | -72.29 | 39.27 | 21.22 |
| | Nuclear | -69.15 | 0.0 | 0.0 | -69.15 | -69.15 | 0.0 | 0.0 | -69.15 |
| | DFT XC | 0.0 | 0.0 | 9.26 | 9.26 | 0.0 | 0.0 | 10.03 | 10.03 |
| | Total | 98.83 | -199.44 | 106.79 | 6.18 | 93.22 | -197.11 | 109.51 | 5.62 |

Table S2: Contributions of $K_0$, $K_v$ and $K_e$ to the force constant of the orbital $1a''_2$ $NH_3$ and their decomposition in kinetic energy ($T$), electron-electron repulsion ($V_{ee}$), electron-nuclear interactions ($V_{en}$) at GGA (BLYP and PBE)/cc-pvtz level of theory. Units are eV/Å$^2$.

| | | $k_0$ | $2k_v$ | $k_e$ | $k$ |
|---|---|---|---|---|---|
| BLYP | $T$ | 125.05 | -308.90 | 178.27 | -5.58 |
| | $V_{en}$ | 94.13 | -51.65 | -22.47 | 20.01 |
| | $V_{ee}$ | -47.35 | 38.00 | -8.58 | -17.93 |
| | Total | 171.84 | -322.55 | 147.23 | -3.50 |
| PBE | $T$ | 126.18 | -310.92 | 167.03 | -17.71 |
| | $V_{en}$ | 94.11 | -51.31 | 2.99 | 45.79 |
| | $V_{ee}$ | -51.61 | 38.15 | -16.44 | -29.90 |
| | Total | 168.69 | -324.09 | 153.58 | -1.82 |