**Pseudosymmetry Analysis of the d-block Molecular Orbitals**

**in Four-coordinate Complexes**

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**Supporting Information**

**Table S1.** Pseudosymmetry representation decomposition of the $z^2$ and $x^2$-$y^2$-based MOs for the series of $[Ni^{II}(PH_3)_3X]$ complexes, and products of coefficients involved in equation 11.

| $z^2$ | $PH_3$ | Br | Cl | F | Me | $NH_3$ | CN |
|---|---|---|---|---|---|---|---|
| $\omega(A_{1g})$ | 0.994 | 0.984 | 0.988 | 0.974 | 0.910 | 0.995 | 0.919 |
| $\omega(A_{2g})$ | 0.002 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.000 |
| $\omega(B_{1g})$ | 0.000 | 0.001 | 0.002 | 0.009 | 0.020 | 0.002 | 0.014 |
| $\omega(B_{2g})$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| $\omega(E_g)$ | 0.004 | 0.005 | 0.000 | 0.000 | 0.013 | 0.000 | 0.042 |
| $\omega(A_{2u})$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.002 |
| $\omega(B_{2u})$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.001 | 0.002 |
| $\omega(E_u)$ | 0.000 | 0.010 | 0.010 | 0.017 | 0.051 | 0.001 | 0.022 |

| $x^2$-$y^2$ | $PH_3$ | Br | Cl | F | Me | $NH_3$ | CN |
|---|---|---|---|---|---|---|---|
| $\omega(A_{1g})$ | 0.000 | 0.010 | 0.018 | 0.059 | 0.035 | 0.018 | 0.064 |
| $\omega(A_{2g})$ | 0.000 | 0.000 | 0.001 | 0.000 | 0.003 | 0.000 | 0.000 |
| $\omega(B_{1g})$ | 0.974 | 0.945 | 0.928 | 0.808 | 0.803 | 0.934 | 0.803 |
| $\omega(B_{2g})$ | 0.018 | 0.001 | 0.001 | 0.001 | 0.048 | 0.006 | 0.001 |
| $\omega(E_g)$ | 0.000 | 0.006 | 0.000 | 0.001 | 0.005 | 0.002 | 0.030 |
| $\omega(A_{1u})$ | 0.000 | 0.001 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| $\omega(A_{2u})$ | 0.000 | 0.001 | 0.000 | 0.001 | 0.021 | 0.004 | 0.004 |
| $\omega(B_{1u})$ | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $\omega(B_{2u})$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.003 |
| $\omega(E_u)$ | 0.007 | 0.035 | 0.052 | 0.130 | 0.083 | 0.035 | 0.094 |

**a** = $\omega(A_{1g}, z^2)\cdot\omega(E_u, x^2\text{-}y^2)$
b = $\omega(B_{1g}, z^2)\cdot\omega(E_u, x^2\text{-}y^2)$
c = $\omega(E_u, z^2)\cdot\omega(A_{1g}, x^2\text{-}y^2)$
**d** = $\omega(E_u, z^2)\cdot\omega(B_{1g}, x^2\text{-}y^2)$

| Product | $PH_3$ | Br | Cl | F | Me | $NH_3$ | CN |
|---|---|---|---|---|---|---|---|
| **a** | **0.007** | **0.034** | **0.051** | **0.127** | **0.076** | **0.035** | **0.086** |
| b | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | 0.000 | 0.001 |
| c | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | 0.000 | 0.001 |
| **d** | **0.000** | **0.009** | **0.009** | **0.014** | **0.041** | **0.001** | **0.018** |