# Supporting information

of the communication

# Experimental and Theoretical Charge density studies at sub-atomic resolution

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**Table S1. Experimental and theoretical structure factors of Diamond (sin $\theta/\lambda \leq 1.45$ Å$^{-1}$)**

| h | k | l | $F_{obs}$(300K)[a] | $F^{sta}$(W2K)[c] | Pendel.[g] |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 18.54(12) | 18.6097 | 18.37(6) |
| 2 | 0 | 2 | 15.35(15 | 15.7828 | 15.36(4) |
| 1 | 1 | 3 | 9.21(9) | 9.5954 | 9.32(2) |
| 2 | 2 | 2 | 0.91(4)[b] | 0.9024 | 1.15(8) |
| 0 | 0 | 4 | 11.83(4) | 12.5149 | 11.93(5) |
| 3 | 1 | 3 | 8.42(8) | 8.8261 | 8.39(4) |
| 2 | 2 | 4 | 10.83(11) | 11.5131 | 10.90(8) |
| 3 | 3 | 3 | 7.19(7) | 7.7607 | 7.28(3) |
| 1 | 1 | 5 | 7.26(7) | 7.8658 | 7.41(1) |
| 4 | 0 | 4 | 9.70(10) | 10.5910 | 9.58(2) |
| 3 | 1 | 5 | 6.57(7) | 7.2262 | |
| 4 | 2 | 4 | -[b] | 0.0686 | |
| 2 | 0 | 6 | 8.70(9) | 9.7448 | |
| 3 | 3 | 5 | 6.04(6) | 6.7362 | |
| 2 | 2 | 6 | -[b] | 0.0357 | |
| 4 | 4 | 4 | 8.00(9) | 9.0309 | |
| 1 | 1 | 7 | 5.38(5) | 6.1886 | |
| 5 | 1 | 5 | 5.40(6) | 6.2172 | |
| 4 | 2 | 6 | 7.16(7) | 8.3753 | |
| 5 | 3 | 5 | 4.88(5) | 5.7492 | |
| 3 | 1 | 7 | 4.89(5) | 5.7696 | |
| 0 | 0 | 8 | 6.40(9) | 7.7761 | |
| 3 | 3 | 7 | 4.48(5) | 5.3478 | |
| 4 | 4 | 6 | -[b] | 0.0116 | |
| 2 | 2 | 8 | 5.94(6) | 7.2547 | |
| 6 | 0 | 6 | 5.95(6) | 7.2568 | |
| 5 | 5 | 5 | 4.11(4) | 5.0042 | |
| 5 | 1 | 7 | 4.10(4) | 4.9969 | |
| 6 | 2 | 6 | -[b] | 0.0059 | |
| 4 | 0 | 8 | 5.44(6) | 6.7769 | |
| 1 | 1 | 9 | 3.73(4) | 4.6717 | |
| 5 | 3 | 7 | 3.73(4) | 4.6774 | |
| 4 | 2 | 8 | -[b] | 0.0063 | |
| 6 | 4 | 6 | 5.05(6) | 6.3410 | |
| 3 | 1 | 9 | 3.40(3) | 4.3744 | |
| 4 | 4 | 8 | 4.55(6) | 5.9455 | |
| 7 | 1 | 7 | 3.14(4) | 4.1060 | |
| 3 | 3 | 9 | 3.14(4) | 4.1064 | |
| 5 | 5 | 7 | 3.14(4) | 4.1008 | |
| 6 | 2 | 8 | 4.25(5) | 5.5852 | |
| 2 | 0 | 10 | 4.25(5) | 5.5848 | |
| 7 | 3 | 7 | 2.89(4) | 3.8573 | |
| 5 | 1 | 9 | 2.89(4) | 3.8597 | |

[a] observed structure factors at room temperature (this study), [b] systematically absent reflections. [c] calculated structure factors based on the Wien2K (ref 2) calculation employing the PBE GGA-functional (this study), [d] calculated structure factors using Crystal06 (ref 3) at PBE/6-311G3d level of approximation, [e] thermal convoluted structure factors based on the Wien2K calculations and assuming an $U_{iso}$ value of 0.00178, [f] thermal convoluted structure factors calculated using the Crystal06 calculations an assuming an Uiso value of 0.00176, [g] Single crystal data based on the Pendellösung method (ref 4).

## S2. Multipolar refinements and AIM analyses employing various static theoretical structure factors ($F^{sta}$)

In order to test the influence of the basis set employed for the structure factor calculations and subsequent multipolar refinements several electronic structure calculations were performed using the LCAO approach and the B3PW [5, 6] functional as implemented in Crystal06 (C06) [3]. The calculations were performed using a tight radial and angular quadrature with 455 points inside the Brillouin zone. In order to assist the SCF convergence, the eigenvalue level shifting technique was used. The structure factors were calculated using split-valence Gaussian type orbitals (GTO) with and without polarization functions: 6-31G, 6-311G, 6-31G(d), 6-311G(d), 6-311G(2d), 6-311G(3d), 6-311G(3df). The Gaussian coefficients were taken from literature [7, 8, 9, 10] and subsequently contracted in order to avoid any basis set linear dependence error and an unphysical conducting state for diamond (see S7).

The reconstruction of the theoretical charge density by multipolar refinements was performed using the XD program [11]. The SCM scattering data bank obtained from relativistic Dirac–Fock calculations of Su, Coppens and Macchi (SCM) [12, 13] was used throughout. The radial functions (RF) of an $sp^3$ hybridized carbon atoms (denoted Cv in the SCM database) and an averaged single $\zeta$ density value in accord with the presumed $sp^3$-configuration was employed. All multipolar refinements were performed at a resolution of $\sin\theta/\lambda = 1.45$ Å$^{-1}$ to allow detailed studies of core expansion/contraction and polarization effects. Two independent multipolar functions (O2-, H0) were allowed by symmetry up to fourth order on the carbon atom, while the third hexadecapole H4+ was constrained to H0 by H4+ = (0.74045)H0. The local coordinate system was oriented such that a positive sign of the multipole term O2- signals a charge accumulation between a carbon atom at (0, 0, 0) and its nearest bonding neighbours. The fractional multipoles were multiplied by their site multiplicity (24). The anomalous dispersion factors were set to zero, the scale factor was fixed to unity and refinements were performed against $F$-values and unit weights were used throughout. The isotropic thermal displacement parameter was kept at zero and the core kappa ($\kappa_{core}$) and core population parameter $P_c$ were refined.

**Table S3. Comparison of Multipolar Refinements based on LCAO calculations using Crystal06, LAPW calculations employing Wien2K and PAW calculations**

| | 6-31G | 6-311G | 6-311G(d) | 6-311G(2d) |
|---|---|---|---|---|
| $R_1$ | 0.0008 | 0.0013 | 0.0011 | 0.0006 |
| $\Delta\rho(\mathbf{r})$ [eÅ$^{-3}$] | -0.030<br>0.017 | -0.044<br>0.024 | -0.034<br>0.026 | -0.028<br>0.013 |
| $\kappa_{valence}$ | 0.9623 | 0.9863 | 0.9809 | 0.9750 |
| $\kappa'_{deformation}$ | 0.794 | 0.825 | 0.890 | 0.876 |
| $P_{valence}$ | 4.021 | 4.029 | 4.025 | 4.026 |
| $\kappa_{core}$ | 1.0109 | 1.0144 | 1.0124 | 1.0105 |
| $P_{\mathrm{core}}$ | 1.979 | 1.971 | 1.975 | 1.979 |
| O2- | 0.307 | 0.245 | 0.314 | 0.332 |
| H0 | -0.154 | -0.113 | -0.094 | -0.098 |
| $\rho(\mathbf{r})_{\mathrm{BCP}}$ [eÅ$^{-3}$] | 1.527 | 1.474 | 1.585 | 1.593 |
| $\nabla^2\rho(\mathbf{r})_{\mathrm{BCP}}$ [eÅ$^{-5}$] | -9.190 | -7.172 | -10.552 | -10.898 |
| $\lambda_1$ [eÅ$^{-5}$] | -8.98 | -8.65 | -10.13 | -10.12 |
| $\lambda_2$ [eÅ$^{-5}$] | -8.97 | -8.64 | -10.12 | -10.11 |
| $\lambda_3$ [eÅ$^{-5}$] | 8.77 | 10.11 | 9.70 | 9.33 |

| | 6-311G(3d) | 6-311G(3df) | W2K(HC+$\kappa_{\mathrm{core}}$)[a] | PAW (HC+$\kappa_{\mathrm{core}}$)[b] |
|---|---|---|---|---|
| $R_1$ | 0.0006 | 0.0004 | 0.0005 | 0.0006 |
| $\Delta\rho(\mathbf{r})$ [eÅ$^{-3}$] | -0.017<br>0.021 | -0.011<br>0.012 | -0.01<br>0.02 | -0.018<br>0.015 |
| $\kappa_{valence}$ | 0.969 | 0.9681 | 0.970 | 0.9711 |
| $\kappa'_{deformation}$ | 0.857 | 0.862 | 0.872 | 0.860 |
| $P_{valence}$ | 4.0169 | 4.010 | 4.013 | 4.008 |
| $\kappa_{core}$ | 1.0083 | 1.008 | 1.006 | 1.0054 |
| $P_{\mathrm{core}}$ | 1.983 | 1.990 | 1.987 | 1.992 |
| O2- | 0.358 | 0.364 | 0.340 | 0.334 |
| H0 | -0.089 | -0.098 | -0.109 | -0.122 |
| $\rho(\mathbf{r})_{\mathrm{BCP}}$ [eÅ$^{-3}$] | 1.595 | 1.612 | 1.607 | 1.595 |
| $\nabla^2\rho(\mathbf{r})_{\mathrm{BCP}}$ [eÅ$^{-5}$] | -10.924 | -11.550 | -11.534 | -11.199 |
| $\lambda_1$ [eÅ$^{-5}$] | -9.97 | -10.1622 | -10.26 | -10.12 |
| $\lambda_2$ [eÅ$^{-5}$] | -9.95 | -10.21 | -10.26 | -10.11 |
| $\lambda_3$ [eÅ$^{-5}$] | 9.00 | 8.89 | 8.99 | 9.02 |

[a] For comparison reasons the multipolar refinement results based on the Wien2K (ref 2) calculation employing the PBE GGA-functional was included (for details see experimental part of the manuscript). Note, that these results (employing the XD multipolar refinement program) agree well

with the results listed in Table 2 of our paper (based on multipolar refinements using the JANA). The LCAO calculations using split-valence basis sets of double and triple-zeta quality were performed with Crystal06 using the B3PW functional (ref 5, 6); [b] Multipolar refinement including $\kappa_{core}$ and $P_c$ refinements based on the PAW (ref 14) data of ref 1.

## S4. Basis set influence on the topological parameters of diamond (Crystal06 calculations)

The influence of the basis set on the topological parameters was tested employing the minimal (STO*n*G: *n*=2-6) and split-valence Gaussian type orbitals (GTO): 3-21G, 4-31G, 6-21G, 6-31G, 6-311G by direct wave function analysis. GTO structure factors were also calculated adding polarization functions (3-21G(d), 4-31G(d), 6-21G(d), 6-31G(d), 6-311G(d), 6-311G(2d), 6-311G(3d), 6-311G(3df)). The basis set STO*n*G (*n*=2-6), 3-21G, 3-21G(d), 6-21G, 6-21G(d) were used with the standard coefficient implemented inside the Crystal06 code. For the 4-31G, 4-31G(d), 6-31G, 6-31G(d), 6-311G, 6-311G(d), 6-311G(2d), 6-311G(3d) and 6-311G(3df) bases the coefficients were taken from literature [7, 8, 9, 10] and subsequently contracted in order to avoid any basis set linear dependence error and an unphysical conducting state for diamond (see S7). All the calculation were made using the B3PW [5, 6] functional.

### Table S4a. STO*n*G/ B3PW level of approximation

| STO*n*G | $\rho(\mathbf{r})_{bcp}$ [a] | $\nabla^2\rho(\mathbf{r})_{bcp}$ [a] | $\lambda_3$ [a] | $\nabla^2\rho(\mathbf{r})_{BCC}$ [a] |
|---|---|---|---|---|
| STO2G | 0.230 | -0.363 | 0.477 | -1.096 |
| STO3G | 0.241 | -0.616 | 0.185 | -6.392 |
| STO4G | 0.234 | -0.427 | 0.376 | -8.677 |
| STO5G | 0.236 | -0.529 | 0.276 | -7.366 |
| STO6G | 0.235 | -0.478 | 0.321 | -8.064 |

[a] All values in a.u.

### Table S4b. DZ/B3PW level of approximation (DZ: split-valence basis sets of double-zeta quality)

| GTO DZ | $\rho(\mathbf{r})_{bcp}$ [a] | $\nabla^2\rho(\mathbf{r})_{bcp}$ [a] | $\lambda_3$ [a] | $\nabla^2\rho(\mathbf{r})_{BCC}$ [a] |
|---|---|---|---|---|
| 3-21G | 0.230 | -0.556 | 0.213 | -0.543 |
| 4-31G | 0.227 | -0.405 | 0.353 | -0.783 |
| 6-21G | 0.230 | -0.562 | 0.213 | -0.564 |
| 6-31G | 0.227 | -0.392 | 0.368 | -0.764 |

[a] All values in a.u.

**Table S4c. DZ+P/B3PW level of approximation (DZ+P: split-valence basis sets of double-zeta quality and additional polarization functions)**

| GTO DZ polarize | $\rho(\mathbf{r})_{bcp}$ [a] | $\nabla^2\rho(\mathbf{r})_{bcp}$ [a] | $\lambda_3$ [a] | $\nabla^2\rho(\mathbf{r})_{BCC}$ [a] |
|---|---|---|---|---|
| 3-21G(d) | 0.248 | -0.734 | 0.176 | -0.740 |
| 4-31G(d) | 0.243 | -0.560 | 0.324 | -0.974 |
| 6-21G(d) | 0.249 | -0.743 | 0.176 | -0.749 |
| 6-31G(d) | 0.243 | -0.536 | 0.341 | -0.940 |

[a] All values in a.u.

**Table S4d. TZ+P/B3PW level of approximation (TZ+P: split-valence basis sets of triple-zeta quality and additional polarization functions)**

| GTO TZ | $\rho(\mathbf{r})_{bcp}$ [a] | $\nabla^2\rho(\mathbf{r})_{bcp}$ [a] | $\lambda_3$ [a] | $\nabla^2\rho(\mathbf{r})_{BCC}$ [a] |
|---|---|---|---|---|
| 6-311G | 0.220 | -0.345 | 0.414 | -0.699 |
| 6-311G(d) | 0.238 | -0.507 | 0.386 | -0.891 |
| 6-311G(2d) | 0.238 | -0.489 | 0.392 | -0.908 |
| 6-311G(3d) | 0.238 | -0.496 | 0.375 | -0.881 |
| 6-311G(3df) | 0.237 | -0.487 | 0.376 | -0.912 |

[a] All values in a.u.

## S5. Influence of the DFT functional on the topological parameters in Diamond.

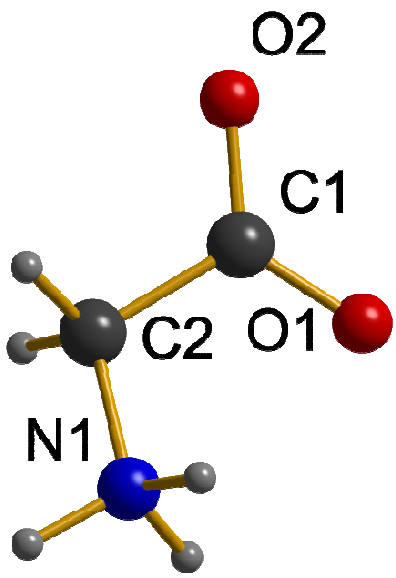
The Hartree-Fock(HF) level of theory was compared with the DFT one using different functionals (BPW [15, 6], B3PW [5, 6], BLYP [15, 16], B3LYP [5, 16], PBE 17, PBE0 18). All those calculation were made using the 6-21G(d) basis set.

| 6-21G(d) | $\rho(\mathbf{r})_{bcp}$ [a] | $\nabla^2\rho(\mathbf{r})_{bcp}$ [a] | $\lambda_3$ [a] | $\nabla^2\rho(\mathbf{r})_{BCC}$ [a] |
|---|---|---|---|---|
| HF | 0.261 | -0.865 | 0.131 | -0.870 |
| BPW | 0.246 | -0.715 | 0.187 | -0.719 |
| B3PW | 0.249 | -0.743 | 0.176 | -0.749 |
| BLYP | 0.249 | -0.729 | 0.195 | -0.734 |
| B3LYP | 0.251 | -0.756 | 0.182 | -0.760 |
| PBE | 0.246 | -0.712 | 0.186 | -0.716 |
| PBE0 | 0.250 | -0.750 | 0.173 | -0.754 |

[a] All values in a.u.

**S6. Topological analysis of α-Glycine based on direct wave function analyses and charge densities recovered from the theoretical structure factors, $F^{sta}$, via multipolar refinements.**

The electronic structure of the α-glycine based on its experimental geometry[19] was calculated using ADF code [20, 21] at QZ4P level using the BLYP [15, 16] functional. The static theoretical structure factors $F^{sta}$ were calculated up to a resolution of $\sin\theta/\lambda$ = 1.80 Å$^{-1}$ employing the DenProp code.[22] The multipolar refinements as described in the paper were based on the $F^{sta}$ values and subsequent topological analyses were performed with JANA2006.[23]




| C1-O2 $_{bcp}$ [a] | ADF | JANA | C1-C2 $_{bcp}$ | ADF | JANA |
|---|---|---|---|---|---|
| $\rho(\mathbf{r})$ | 2.62 | 2.63 | $\rho(\mathbf{r})$ | 1.68 | 1.65 |
| $\nabla^2\rho(\mathbf{r})$ | -21.11 | -28.05 | $\nabla^2\rho(\mathbf{r})$ | -14.27 | -11.16 |
| $\lambda_3$ | 24.95 | 15.30 | $\lambda_3$ | 9.58 | 11.82 |
| ε | 0.13 | 0.07 | ε | 0.08 | 0.10 |
| C1-O1 $_{bcp}$ | ADF | JANA | N1-C2 $_{bcp}$ | ADF | JANA |
| $\rho(\mathbf{r})$ | 2.61 | 2.63 | $\rho(\mathbf{r})$ | 1.60 | 1.59 |
| $\nabla^2\rho(\mathbf{r})$ | -19.93 | -27.38 | $\nabla^2\rho(\mathbf{r})$ | -12.60 | -9.85 |
| $\lambda_3$ | 26.97 | 16.63 | $\lambda_3$ | 8.12 | 11.83 |
| ε | 0.11 | 0.07 | ε | 0.03 | 0.04 |

[a] Salient topological parameters for α-glycine; $\rho(\mathbf{r})$ in e/Å$^3$, $\nabla^2\rho(\mathbf{r})$ and $\lambda_3$ in e/Å$^5$.

## S7. Basis sets employed for the Crystal06 calculation.

The calculation was performed increasing the normal accuracy used by Crystal06. 201 points were used to define the radial grid whereas the angular one was composed by five intervals: 0 – 2.3 Å, 2.3 – 2.4 Å, 2.4 – 2.6 Å, 2-6 – 2.8 Å, 2.8 – 9999.0 Å. The Lebedev quadrature used inside of each interval was 29, 20, 13, 11 and 1 respectively.

### 4-31G

```
6  3
0 0 4  2.0  1.0
486.96693          0.0177258
73.371094          0.1234787
16.413458          0.4338754
4.3449836          0.5615042
0 1 3  4.0  1.0
8.6735253         -0.1213837        0.0635454
2.0966193         -0.2273385        0.2982678
0.6046513          1.1851739        0.7621032
0 1 1  0.0  1.0
0.1835578          1.0              1.0
```

### 4-31G(d)

```
6  4
0 0 4  2.0  1.0
486.96693          0.0177258
73.371094          0.1234787
16.413458          0.4338754
4.3449836          0.5615042
0 1 3  4.0  1.0
8.6735253         -0.1213837        0.0635454
2.0966193         -0.2273385        0.2982678
0.6046513          1.1851739        0.7621032
0 1 1  0.0  1.0
0.1835578          1.0              1.0
0 3 1  0.0  1.0
0.8                1.0
```

### 6-31G

```
6  3
0 0 6  2.0  1.0
3047.5249          0.0018347
457.36951          0.0140373
103.94869          0.0688426
29.210155          0.2321844
9.2866630          0.4679413
3.1639270          0.3623120
0 1 3  4.0  1.0
7.8682724         -0.1193324        0.0689991
1.8812885         -0.1608542        0.3164240
0.5442493          1.1434564        0.7443083
0 1 1  0.0  1.0
0.1787144          1.0              1.0
```

## 6-31G(d)

```
6  4
0 0 6  2.0  1.0
3047.5249          0.0018347
457.36951          0.0140373
103.94869          0.0688426
29.210155          0.2321844
9.2866630          0.4679413
3.1639270          0.3623120
0 1 3  4.0  1.0
7.8682724         -0.1193324        0.0689991
1.8812885         -0.1608542        0.3164240
0.5442493          1.1434564        0.7443083
0 1 1  0.0  1.0
0.1787144          1.0              1.0
0 3 1  0.0  1.0
0.8                1.0
```

## 6-311G

```
6  4
0 0 6  2.0  1.0
4563.2400          0.00196665
682.02400          0.0152306
154.97300          0.0761269
44.455300          0.2608010
13.029000          0.6164620
1.8277300          0.2210060
0 1 3  4.0  1.0
20.964200          0.1146600        0.0402487
4.8033100          0.9199990        0.2375940
1.4593300         -0.00303068       0.8158540
0 1 1  0.0  1.0
0.5934560          1.0              1.0
0 1 1 0.0   1.0
0.1755850          1.0              1.0
```

## 6-311G(d)

```
6  5
0 0 6  2.0  1.0
4563.2400          0.00196665
682.02400          0.01523060
154.97300          0.07612690
44.455300          0.26080100
13.029000          0.61646200
1.8277300          0.22100600
0 1 3  4.0  1.0
20.964200          0.11466000       0.0402487
4.8033100          0.91999900       0.2375940
1.4593300         -0.00303068       0.8158540
0 1 1  0.0  1.0
0.5934560          1.0              1.0
0 1 1  0.0  1.0
0.1955850          1.0              1.0
0 3 1  0.0  1.0
0.7560000          1.0
```

## 6-311G(2d)

```
6  6
0 0 6  2.0 1.0
4563.240            0.00196665
682.0240            0.0152306
154.9730            0.0761269
44.45530            0.2608010
13.0290000          0.6164620
1.8277300           0.2210060
0 1 3  4.0  1.0
20.96420             0.1146600         0.0402487
4.803310             0.9199990         0.2375940
1.459330            -0.00303068        0.8158540
0 1 1  0.0  1.0
0.5234560             1.0              1.0
0 1 1  0.0  1.0
0.1955850             1.0              1.0
0 3 1  0.0  1.0
1.85                  1.0
0 3 1  0.0  1.0
0.71                  1.0
```

## 6-311G(3d)

```
6  7
0 0 6  2.0  1.0
4563.2400             0.00196665
682.02400             0.0152306
154.97300             0.0761269
44.455300             0.2608010
13.029000             0.6164620
1.8277300             0.2210060
0 1 3  4.0  1.0
20.964200             0.1146600        0.0402487
4.8033100             0.9199990        0.2375940
1.4593300            -0.00303068       0.8158540
0 1 1  0.0  1.0
0.5034560             1.0              1.0
0 1 1  0.0  1.0
0.305850              1.0              1.0
0 3 1  0.0  1.0
3.00                  1.0
0 3 1  0.0  1.0
0.95                  1.0
0 3 1  0.0  1.0
0.45                  1.0
```

## 6-311G(3df)

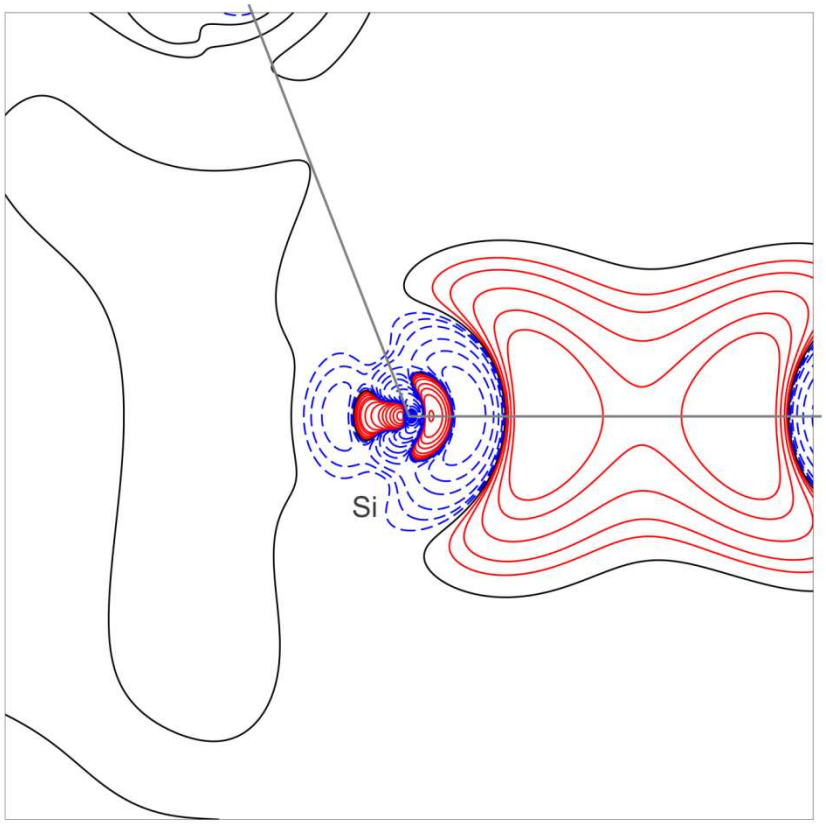
```
6  8
0 0 6  2.0  1.0
4563.240              0.00196665
682.0240              0.0152306
154.9730              0.0761269
44.45530              0.2608010
13.02900              0.6164620
1.827730              0.2210060
0 1 3  4.0  1.0
20.9642000            0.1146600        0.0402487
4.8033100             0.9199990        0.2375940
1.4593300            -0.00303068       0.8158540
0 1 1  0.0  1.0
0.5034560             1.0              1.0
0 1 1  0.0  1.0
0.305850              1.0              1.0
0 3 1  0.0  1.0
3.00                  1.0
0 3 1  0.0  1.0
0.95                  1.0
0 3 1  0.0  1.0
0.45                  1.0
0 4 1  0.0  1.0
1.15                  1.0
```

**Table S8. Multipole parameters and refinement results based on theoretical $F^{sta}$ values (Wien2K)**

| | W2K (HC)[a] | W2K (HC+$U_{iso}$)[a] | W2K (HC+$\kappa_{core}$)[a] | W2K (HC+$\kappa_{core}$)[b] |
|---|---|---|---|---|
| $R_1$ | 0.004 | 0.0015 | 0.0011 | 0.0005 |
| $\Delta\rho(\mathbf{r})$ [eÅ$^{-3}$] | 0.22 | 0.03 | 0.03 | 0.02 |
| | -0.12 | -0.03 | -0.02 | -0.01 |
| $U_{iso}$ | 0.0[c] | -0.000117 | 0.0[c] | 0.0[c] |
| scale | 1.0024 | 0.9934 | 1.0[c] | 1.0[c] |
| $\kappa_{valence}$ | 0.947 | 0.965 | 0.969 | 0.970 |
| $\kappa'_{deformation}$ | 0.808 | 0.812 | 0.819 | 0.873 |
| $P_v$ | 4.0[c] | 4.0[c] | 4.021 | 4.013 |
| $\kappa_{core}$ | 1.0[c] | 1.0[c] | 1.0139 | 1.006 |
| $P_c$ | 2.0[c] | 2.0[c] | 1.979 | 1.987 |
| O2- | 0.42 | 0.423 | 0.410 | 0.338 |
| H0 | -0.20 | -0.177 | -0.163 | -0.108 |
| $\rho(\mathbf{r})_{BCP}$ [eÅ$^{-3}$] | 1.63 | 1.62 | 1.61 | 1.60 |
| $\nabla^2\rho(\mathbf{r})_{BCP}$ [eÅ$^{-5}$] | -13.6 | -12.8 | -12.4 | -11.5 |
| $\lambda_3$ [eÅ$^{-5}$] | 7.0 | 7.8 | 8.1 | 9.0 |
| $\nabla^2\rho(\mathbf{r})_{BCC}$ [eÅ$^{-5}$] | -19.9 | -19.6 | -20.0 | -21.6 |

[a] multipolar refinements based on the radial functions of a free carbon atom ($s^2p^2$ configuration, $^3P$ state; VM data base); [b] Core kappa refinement including the adoption of the core population $P_c$ and employing the radial functions of an $sp^3$ hybridized carbon atom (SCM data base) ; [c] unrefined value.

**Figure S9. Isocontour map of *L*(r) of the electron density distribution of one of the four Si-Si bonding NBOs in $Si(SiH_3)_4$. Contour values at default AIM values as specified in the manuscript.**



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