Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information for: "The interplay of density functional selection and crystal structure for accurate NMR chemical shift predictions"

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Note: Crystal structures (CIF format) for all structures analyzed in this study are provided as separate files. For convenience, XYZ-format files containing the monomer geometries used to compute the monomer corrections to the chemical shielding are also included. Those monomer structures were extracted directly from the optimized crystal structures.

S1 ^{13}C and ^{15}N benchmark datasets

S1.1 List of crystal structures included in the ^{13}C and ^{15}N datasets

Tables S1 and S2 list the Cambridge Structure Database (CSD) reference codes and molecule names for the crystal structures in the ^{13}C and ^{15}N benchmark datasets. All experimental crystal structures were obtained at room temperature, except CYSCLM11 (203 K) and FUSVAQ01 (105 K). For both CYSCLM11 and FUSVAQ01, the difference in lattice constants between the chosen structure and room temperature is 0.1 Å or less. See ref 1 for additional discussion of the FUSVAQ01 structure.

Table S1: CSD Reference codes for the 21 crystal structures included in the ^{13}C dataset

RefCode	**Name**
ADENOS12	Adenosine
ASPARM03	L-Asparagine monohydrate
FRUCTO02	β-D-Fructopyranose
GLUTAM01	L-Glutamine
GLYCIN29	Glycine
HXACAN26	Acetaminophen
LALNIN12	L-Alanine
LCYSTN21	L-Cysteine
LSERIN01	L-Serine
LSERMH10	L-Serine monohydrate
LTHREO01	L-Threonine
LTYROS11	L-Tyrosine
MBDGAL02	Methyl-β-D-galactopyranoside
MEMANP11	Methyl-α-D-manopyranoside
MGALPY01	Methyl-α-D-galactopyranoside monohydrate
MGLUCP11	Methyl-α-D-glucopyranoside
PERYTO10	Pentaerythrytol
RHAMAH12	α-L-Rhamnose monohydrate
SUCROS04	Sucrose
SULAMD06	4-Aminobenzenesulfonamide
TRIPHE11	Triphenylene

Table S2: CSD Reference codes for the 15 crystal structures included in the ^{15}N dataset

RefCode	**Name**
BAPLOT01	Theophylline
BITZAF	Pyridoxine
CIMETD	Cimetidine
CYSCLM11	L-Cysteine hydrochloride monohydrate ($T = 203$ K)
CYTSIN	Cytosine
FUSVAQ01	Adenine trihydrate ($T = 105$ K)
GEHHEH	*N*-(Pyridoxylidenium)tolylamine 2-nitrobenzoate
GEHHIL	*N*-(Pyridoxlidene)methylamine
GLYCIN03	Glycine
LHISTD02	L-Histidine (monoclinic)
LHISTD13	L-Histidine (orthorhombic)
LTYRHC10	L-Tyrosine hydrochloride
TEJWAG	L-Histidine glycolate
THYMIN01	Thymine
URACIL	Uracil

S1.2 Comparison of DFT and experimental crystal structures

Tables S3 and S4 list the rmsd15 errors[2] for the DFT-optimized crystal structures relative to the experimental ones. The lattice parameters were constrained to their experimental values during the structure optimizations, and hydrogen atoms were excluded from the rmsd15 comparison.

Table S3: The rmsd15 errors (Å) computed from overlays of the DFT-optimized and experimental crystal structures in the ^{13}C test set (fixed lattice parameter optimizations).

RefCode	PBE-D3(BJ) Structures	PBE0-D3(BJ) Structures
ADENOS12	0.043	0.028
ASPARM03	0.022	0.029
FRUCTO02	0.043	0.056
GLUTAM01	0.056	0.037
GLYCIN29	0.302	0.268
HXACAN09	0.119	0.090
INDMET	0.133	0.150
LALNIN12	0.029	0.025
LCYSTN21	0.590	0.067
LSERIN01	0.036	0.029
LSERMH10	0.081	0.066
LTHREO01	0.039	0.077
LTYROS11	0.286	0.270
MBDGAL02	0.085	0.119
MEMANP11	0.049	0.066
MGALPY01	0.088	0.066
MGLUCP11	0.138	0.126
PERYTO10	0.034	0.036
RHAMAH12	0.033	0.040
SUCROS04	0.032	0.048
SULAMD06	0.131	0.155
TRIPHE11	0.486	0.547
Mean	**0.130**	**0.109**

Table S4: The rmsd15 errors (Å) computed from overlays of the DFT-optimized and experimental crystal structures in the ^{15}N test set (fixed lattice parameter optimizations).

RefCode	PBE-D3(BJ) Structures	PBE0-D3(BJ) Structures
BAPLOT01	0.214	0.008
BITZAF	0.357	0.312
CIMETD	0.109	0.092
CYSCLM11	0.122	0.102
CYTSIN	0.186	0.182
FUSVAQ01	0.028	0.029
GEHHEH	0.332	0.364
GEHHIL	0.097	0.133
GLYCIN03	0.238	0.264
LHISTD02	0.050	0.048
LHISTD13	0.080	0.088
LTYRHC10	0.106	0.110
TEJWAG	0.077	0.053
THYMIN01	0.125	0.125
URACIL	0.167	0.170
Mean	**0.153**	**0.140**

S1.3 Experimental and calculated chemical shifts for the ^{13}C dataset

Tables S5 and S6 list the experimental and computed chemical shifts (ppm) for the ^{13}C dataset for structures optimized with the PBE-D3(BJ) and PBE0-D3(BJ) functionals, respectively. The structure optimizations were constrained to retain the experimental lattice parameters.

Table S5: Experimental and predicted values for the 132 chemical shifts (ppm) in the ^{13}C benchmark dataset, as computed with GIPAW PBE and after monomer-correction with various functionals. The crystal structures were optimized with PBE-D3(BJ).

^{13}C Chemical Shifts (ppm) using PBE-D3(BJ) Structures

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
ADENOS12	154.1	153.6	152.4	154.9	155.2	153.3
	147.9	146.5	146.9	147.4	148.1	147.6
	119.3	120.9	120.2	120.2	120.2	121.6
	154.7	151.0	152.1	152.8	154.0	154.9
	137.4	136.3	135.9	138.9	139.7	137.5
	91.9	96.2	95.6	92.9	92.3	94.5
	74.6	77.2	76.5	75.3	74.8	75.8
	70.9	73.6	73.1	71.8	71.4	72.2
	84.5	87.1	85.8	84.8	84.2	85.8
	62.5	62.8	62.4	62.2	61.9	61.9
ASPARM03	176.4	178.0	178.3	178.6	178.4	178.3
	51.8	49.1	50.0	51.7	52.2	51.3
	36.1	32.0	33.4	34.9	35.4	33.5
	177.1	173.6	173.9	174.7	174.8	174.5
FRUCTO02	65.4	65.6	65.6	65.4	65.4	65.8
	99.7	107.2	106.2	102.4	101.2	103.6
	67.2	68.4	68.3	67.3	66.9	67.4
	69.0	68.6	68.2	67.6	67.1	67.6
	71.4	74.1	73.6	72.3	71.8	72.6
	64.9	66.6	66.5	66.2	66.2	66.6
GLUTAM01	173.0	174.6	174.8	175.6	175.5	174.9
	53.3	52.7	53.6	54.9	55.3	54.6
	25.5	23.3	24.0	25.4	25.8	24.2
	28.5	26.3	28.1	30.0	30.8	28.5
	176.5	174.9	175.3	176.0	176.2	176.0
GLYCIN29	176.2	177.5	178.1	178.7	178.7	178.3
	43.5	39.9	41.7	44.3	45.4	44.0
HXACAN09	133.1	131.2	131.2	131.6	131.9	132.6
	123.4	122.1	122.0	123.5	124.0	123.0
	115.7	113.4	112.8	115.3	115.9	114.8
	152.3	152.5	151.6	150.7	150.3	151.7
	116.4	115.3	114.6	116.5	117.0	116.2
	120.6	118.7	118.3	119.9	120.2	119.1
	169.8	167.9	168.1	169.9	170.3	169.8
	23.8	21.6	23.5	26.3	27.6	25.2
LALNIN12	176.8	179.5	179.5	180.0	179.7	179.5
	50.9	49.0	49.5	51.4	51.8	50.9
	19.8	16.2	17.5	20.2	21.3	19.3
LCYSTN21	174.0	174.4	174.8	175.5	175.4	174.8
	56.7	54.7	55.5	56.8	57.2	56.7
	28.8	29.0	29.1	30.7	30.6	28.5
LSERIN01	175.1	176.3	176.7	177.2	177.1	176.6
	55.6	53.7	54.5	56.1	56.6	56.0
	62.9	65.4	64.9	64.3	64.0	64.1
LSERMH10	175.6	177.2	177.7	178.3	178.1	177.5
	58.3	57.4	58.3	59.4	59.7	59.2
	61.8	62.4	61.8	61.4	61.1	61.1
LTHREO01	171.9	172.2	172.4	173.3	173.3	172.5
	61.2	59.0	59.2	60.5	60.7	60.5

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^{13}C Chemical Shifts (ppm) using PBE-D3(BJ) Structures *(continued)*

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
	66.8	69.4	68.5	68.0	67.5	68.0
	20.4	15.8	17.3	20.1	21.3	19.3
LTYROS11	175.4	176.9	177.2	177.9	177.7	177.1
	130.3	130.3	130.0	131.3	131.6	130.4
	116.4	114.9	114.3	116.0	116.5	116.0
	56.4	55.3	56.0	57.1	57.3	56.7
	131.0	129.4	128.8	130.6	130.9	129.5
	118.0	116.2	115.5	117.7	118.2	117.6
	155.6	156.7	156.0	154.8	154.4	155.8
	36.8	35.0	36.4	36.3	36.4	35.4
	123.6	121.4	120.4	121.6	121.7	121.7
MBDGAL02	105.7	111.2	109.3	105.7	104.3	107.1
	71.2	71.7	71.2	70.2	69.9	70.7
	72.1	74.0	73.4	72.2	71.8	72.7
	69.3	71.6	71.3	70.2	69.8	70.6
	75.6	76.4	75.5	74.7	74.4	75.5
	62.8	63.3	63.2	62.8	62.6	62.6
	57.6	59.3	59.1	60.0	60.4	60.2
MEMANP11	99.6	104.8	103.4	100.1	98.8	101.2
	71.3	72.5	72.1	71.0	70.6	71.5
	71.7	73.5	72.8	71.7	71.1	72.0
	64.8	65.7	65.5	64.8	64.5	64.6
	71.9	74.0	73.3	72.6	72.3	73.2
	58.9	58.5	58.7	58.6	58.7	58.6
	54.9	54.7	54.7	55.9	56.5	56.0
MGALPY01	100.4	105.4	104.2	100.8	99.5	102.0
	67.6	67.7	67.4	66.6	66.2	66.7
	72.6	74.4	73.7	72.9	72.4	73.3
	70.0	71.3	70.9	69.5	69.2	70.2
	72.9	75.3	74.5	73.8	73.5	74.5
	61.4	61.8	61.5	61.3	61.1	61.1
	55.2	54.6	54.6	55.9	56.5	56.0
MGLUCP11	101.0	105.7	104.3	101.0	99.8	102.3
	72.3	71.3	70.8	69.9	69.5	70.3
	74.6	75.8	74.7	73.6	72.9	74.1
	72.5	73.6	72.9	72.0	71.5	72.4
	75.3	74.7	73.7	73.2	72.9	73.9
	63.8	64.0	63.6	63.4	63.1	63.1
	56.5	56.2	56.4	57.4	57.9	57.5
PERYTO10	50.2	49.2	48.6	49.6	49.6	49.1
	58.4	58.9	59.5	59.1	59.0	58.6
RHAMAH12	94.5	100.0	99.0	95.9	94.8	96.8
	72.2	74.2	73.6	72.4	72.0	72.9
	71.0	70.8	70.4	69.6	69.3	69.8
	72.5	73.8	72.8	71.8	71.2	72.0
	69.8	72.3	71.5	71.0	70.7	71.4
	17.8	12.8	15.1	17.8	19.2	17.0
SUCROS04	93.3	97.0	96.4	93.5	92.8	95.0
	66.0	64.4	64.5	64.0	63.9	64.2
	73.7	74.5	74.2	73.1	72.8	73.8
	102.4	108.6	108.0	104.7	103.9	106.4
	72.8	74.3	73.3	72.3	71.7	72.6
	82.9	84.6	83.8	81.7	80.9	82.4
	67.9	68.5	68.2	67.5	67.2	67.7
	71.8	71.9	71.0	70.3	69.8	70.7
	73.6	75.3	74.7	73.8	73.4	74.2
	81.8	81.9	81.0	80.0	79.6	81.0
	60.0	59.5	59.7	59.4	59.4	59.3
	61.0	61.5	61.8	61.5	61.6	61.7
SULAMD06	127.1	127.6	125.6	124.6	123.8	125.9
	129.5	127.7	127.5	130.4	131.1	128.4
	117.1	114.5	113.7	114.9	115.2	115.7
	153.4	149.5	150.2	151.2	152.2	152.5

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^{13}C Chemical Shifts (ppm) using PBE-D3(BJ) Structures *(continued)*

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
	112.3	110.5	109.7	111.1	111.5	111.9
	129.5	127.6	127.4	130.3	130.9	128.3
TRIPHE11	126.4	124.3	123.1	125.1	125.3	124.5
	129.5	129.2	133.7	129.6	129.9	130.1
	124.5	124.2	124.6	125.0	125.3	124.4
	125.9	125.4	124.2	126.1	126.4	125.5
	127.5	125.7	124.4	126.3	126.5	125.6
	122.3	120.0	120.1	121.0	121.2	120.0
	130.2	128.3	132.6	128.5	128.6	128.7
	129.5	127.9	132.1	128.3	128.6	128.7
	120.9	118.4	118.5	119.6	119.8	118.6
	125.9	123.7	122.4	124.4	124.7	123.7
	121.7	119.1	119.4	120.2	120.6	119.4
	129.5	127.8	132.1	128.2	128.7	128.9
	129.5	126.4	130.7	126.8	127.2	127.2
	122.3	121.2	121.5	122.2	122.5	121.5
	126.9	126.3	125.1	126.9	127.1	126.3
	126.9	124.5	123.3	125.3	125.5	124.6
	123.8	124.9	125.4	125.7	125.9	124.9
	129.8	127.6	131.9	127.9	128.2	128.2
RMSE		**2.3**	**2.0**	**1.3**	**1.4**	**1.3**

Table S6: Experimental and predicted values for the 132 chemical shifts (ppm) in the ^{13}C benchmark dataset, as computed with GIPAW PBE and after monomer-correction with various functionals. The crystal structures were optimized with PBE0-D3(BJ).

^{13}C Chemical Shifts using PBE0-D3(BJ) Structures

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
ADENOS12	154.1	153.4	152.2	154.7	155.0	153.2
	147.9	146.7	147.1	147.7	148.3	147.9
	119.3	121.3	120.5	120.6	120.5	121.9
	154.7	151.4	152.6	153.3	154.5	155.3
	137.4	136.0	135.4	138.5	139.2	137.3
	91.9	95.8	95.2	92.6	92.0	94.1
	74.6	76.9	76.2	75.1	74.7	75.6
	70.9	73.3	72.9	71.7	71.3	72.1
	84.5	86.6	85.3	84.3	83.8	85.3
	62.5	63.2	62.7	62.5	62.2	62.2
ASPARM03	176.4	176.5	176.7	176.9	176.8	176.8
	51.8	48.7	49.5	51.2	51.7	50.8
	36.1	32.3	33.7	35.1	35.6	33.7
	177.1	173.4	173.6	174.3	174.5	174.2
FRUCTO02	65.4	65.7	65.7	65.4	65.4	65.8
	99.7	104.8	103.9	100.5	99.5	101.7
	67.2	67.5	67.4	66.5	66.2	66.6
	69.0	68.6	68.1	67.5	67.1	67.6
	71.4	73.6	73.2	71.9	71.4	72.3
	64.9	65.9	65.8	65.5	65.5	65.9
GLUTAM01	173.0	173.2	173.3	174.1	174.0	173.6
	53.3	52.4	53.2	54.4	54.8	54.2
	25.5	23.7	24.4	25.7	26.0	24.6
	28.5	26.5	28.2	30.1	30.8	28.5
	176.5	174.8	175.0	175.7	175.9	175.8
GLYCIN29	176.2	175.9	176.4	176.9	177.0	176.7
	43.5	40.2	41.8	44.3	45.4	44.1
HXACAN09	133.1	131.8	131.7	132.2	132.7	133.2
	123.4	123.3	123.0	124.7	125.2	124.1
	115.7	114.4	113.6	116.3	116.8	115.5
	152.3	152.8	151.7	151.0	150.4	151.6
	116.4	116.5	115.7	117.7	118.1	117.1
	120.6	119.7	119.0	120.8	121.2	119.9
	169.8	167.3	167.3	169.7	170.1	169.3
	23.8	21.7	23.4	26.2	27.4	25.1
LALNIN12	176.8	178.1	178.2	178.5	178.3	178.2
	50.9	48.9	49.5	51.3	51.7	50.8
	19.8	17.1	18.5	21.0	22.1	20.2
LCYSTN21	174.0	172.7	172.9	173.6	173.6	173.1
	56.7	54.6	55.5	56.6	57.1	56.7
	28.8	28.2	28.2	29.9	29.8	27.9
LSERIN01	175.1	174.9	175.0	175.5	175.4	175.1
	55.6	53.7	54.5	56.1	56.6	56.0
	62.9	65.0	64.4	63.9	63.5	63.6
LSERMH10	175.6	175.8	176.1	176.7	176.5	176.2
	58.3	57.4	58.2	59.3	59.6	59.2
	61.8	62.3	61.7	61.3	61.0	61.0
LTHREO01	171.9	170.8	171.0	171.9	171.9	171.3
	61.2	59.0	59.2	60.4	60.6	60.4
	66.8	68.9	68.1	67.6	67.2	67.7
	20.4	17.1	18.6	21.2	22.4	20.6
LTYROS11	175.4	175.3	175.5	176.2	176.0	175.5
	130.3	131.4	131.0	132.3	132.7	131.5
	116.4	115.7	115.0	116.7	117.2	116.6
	56.4	55.3	55.9	57.0	57.2	56.6
	131.0	130.7	130.2	131.9	132.2	130.7
	118.0	116.9	116.2	118.4	118.9	118.2
	155.6	157.2	156.4	155.5	155.1	156.4

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^{13}C Chemical Shifts using PBE0-D3(BJ) Structures *(continued)*

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
	36.8	35.7	37.1	36.8	37.0	36.0
	123.6	122.2	121.2	122.5	122.5	122.5
MBDGAL02	105.7	110.3	108.3	105.0	103.6	106.3
	71.2	71.6	71.0	70.1	69.7	70.5
	72.1	73.9	73.1	72.1	71.6	72.5
	69.3	70.8	70.5	69.5	69.1	69.9
	75.6	76.1	75.2	74.5	74.1	75.2
	62.8	63.6	63.4	63.0	62.8	62.8
	57.6	58.7	58.5	59.4	59.8	59.6
MEMANP11	99.6	103.5	102.1	99.1	97.9	100.1
	71.3	72.4	71.9	71.0	70.6	71.4
	71.7	73.5	72.8	71.7	71.2	72.1
	64.8	64.9	64.8	64.2	63.9	64.0
	71.9	73.3	72.6	71.9	71.6	72.4
	58.9	58.5	58.5	58.5	58.6	58.5
	54.9	54.2	54.3	55.4	56.0	55.5
MGALPY01	100.4	104.1	103.0	99.8	98.6	100.9
	67.6	67.4	67.1	66.3	65.9	66.5
	72.6	73.7	73.1	72.2	71.8	72.6
	70.0	71.2	71.0	69.5	69.2	70.2
	72.9	74.3	73.5	72.8	72.5	73.4
	61.4	62.8	62.4	62.2	61.9	62.0
	55.2	54.4	54.3	55.5	56.1	55.7
MGLUCP11	101.0	104.2	103.0	99.8	98.7	101.1
	72.3	71.1	70.6	69.8	69.5	70.2
	74.6	75.6	74.5	73.4	72.8	74.0
	72.5	73.3	72.6	71.8	71.3	72.2
	75.3	74.3	73.4	72.9	72.6	73.5
	63.8	64.2	63.9	63.6	63.2	63.3
	56.5	56.1	56.3	57.2	57.7	57.3
PERYTO10	50.2	49.3	48.6	49.7	49.7	49.2
	58.4	58.8	59.4	58.9	58.8	58.5
RHAMAH12	94.5	98.5	97.5	94.6	93.6	95.5
	72.2	73.6	73.0	71.9	71.5	72.3
	71.0	71.0	70.5	69.8	69.4	70.0
	72.5	73.5	72.4	71.6	71.0	71.8
	69.8	71.3	70.5	70.1	69.8	70.5
	17.8	13.7	15.8	18.4	19.8	17.7
SUCROS04	93.3	95.4	95.0	92.3	91.6	93.6
	66.0	64.9	65.0	64.5	64.4	64.7
	73.7	74.2	73.8	72.8	72.6	73.5
	102.4	106.3	105.7	102.8	102.1	104.4
	72.8	73.8	72.8	71.9	71.4	72.2
	82.9	85.0	84.3	82.2	81.4	82.9
	67.9	68.4	68.1	67.4	67.1	67.6
	71.8	72.1	71.2	70.5	70.1	70.9
	73.6	74.6	74.1	73.1	72.8	73.5
	81.8	81.8	80.9	79.9	79.5	80.9
	60.0	59.2	59.4	59.2	59.2	59.1
	61.0	61.2	61.5	61.2	61.3	61.4
SULAMD06	127.1	126.8	124.9	124.2	123.5	125.4
	129.5	128.9	128.7	131.5	132.2	129.6
	117.1	115.3	114.4	115.7	115.9	116.3
	153.4	150.6	151.1	152.2	153.1	153.4
	112.3	111.3	110.4	111.9	112.2	112.6
	129.5	128.8	128.6	131.5	132.1	129.6
TRIPHE11	126.4	125.8	124.5	126.5	126.7	125.9
	129.5	130.7	135.3	130.9	131.1	131.3
	124.5	125.7	126.3	126.6	126.8	125.9
	125.9	126.9	125.6	127.6	127.8	126.9
	127.5	126.8	125.5	127.4	127.6	126.7
	122.3	121.2	121.4	122.2	122.4	121.2
	130.2	129.1	133.5	129.2	129.3	129.3

Continued on next page

^{13}C Chemical Shifts using PBE0-D3(BJ) Structures *(continued)*

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
	129.5	128.8	133.2	129.2	129.3	129.4
	120.9	120.3	120.5	121.3	121.5	120.4
	125.9	124.5	123.2	125.2	125.4	124.4
	121.7	120.0	120.4	121.2	121.5	120.4
	129.5	128.8	133.3	129.2	129.7	129.9
	129.5	127.4	131.8	127.7	128.1	128.1
	122.3	122.5	122.8	123.5	123.8	122.7
	126.9	127.7	126.5	128.2	128.4	127.7
	126.9	125.5	124.2	126.1	126.3	125.4
	123.8	126.4	129.4	127.2	127.3	126.3
	129.8	128.4	132.9	128.7	129.0	128.9
RMSE		**1.8**	**1.7**	**1.1**	**1.3**	**0.9**

S1.4 Experimental and calculated chemical shifts for the ^{15}N dataset

Tables S7 and S8 list the experimental and computed shifts for the ^{15}N dataset for structures optimized with the PBE-D3(BJ) and PBE0-D3(BJ) functionals, respectively. The structure optimizations were constrained to preserve the experimental lattice parameters.

Table S7: Experimental and predicted values for the 35 chemical shifts (ppm) in the ^{15}N benchmark dataset, as computed with GIPAW PBE and after monomer-correction with various functionals. The crystal structures were optimized with PBE-D3(BJ).

^{15}N Chemical Shifts (ppm) using PBE-D3(BJ) Structures

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
BITZAF	249.5	244.2	244.1	247.6	248.3	244.9
GEHHEH	187.4	172.9	177.0	175.7	178.3	180.6
	261.0	248.2	249.7	252.8	254.3	253.0
GEHHIL	268.5	271.4	270.5	271.8	271.3	265.2
	261.2	258.1	256.6	259.7	259.7	259.1
LHISTD02	210.8	214.0	214.3	214.4	214.4	215.1
	132.6	136.3	137.5	136.4	137.3	139.3
LHISTD13	210.6	213.4	213.7	213.8	213.8	214.6
	132.4	137.7	139.0	137.7	138.6	140.7
TEJWAG	143.9	145.0	146.3	145.5	146.3	148.2
GLYCIN03	-6.5	-18.4	-18.4	-14.1	-13.0	-14.9
FUSVAQ01	183.2	184.6	183.1	182.7	182.0	185.1
	174.2	172.8	172.4	171.6	171.3	174.0
	192.2	192.7	191.6	193.1	192.5	189.8
	120.2	125.6	126.4	123.9	124.4	126.9
	50.2	47.4	48.0	48.7	49.2	47.6
CYTSIN	110.2	115.2	115.8	112.6	112.1	113.7
	165.2	165.7	164.8	161.6	160.2	163.3
	54.2	48.0	48.1	50.3	51.1	49.5
THYMIN01	90.2	95.0	95.2	92.2	90.9	90.7
	119.2	121.0	120.7	117.5	116.7	118.3
URACIL	96.2	105.2	105.2	102.0	100.6	100.5
	120.2	121.3	120.9	117.5	116.6	118.0
CIMETD	130.5	135.0	136.0	134.6	135.4	137.8
	213.1	214.6	214.8	214.8	214.7	215.1
	56.6	56.7	56.2	57.4	57.5	57.0
	43.5	40.6	38.8	42.1	42.0	40.6
	45.8	39.6	38.6	40.5	40.1	37.7
	149.9	145.0	143.7	146.7	145.8	138.8
BAPLOT01	114.7	123.5	121.4	118.7	116.8	118.6
	72.7	78.7	77.1	76.1	74.4	73.6
	122.7	128.0	129.8	128.3	129.3	131.6
	178.7	180.2	178.9	179.5	179.0	180.1
LTYRHC10	8.0	12.1	12.9	14.0	14.6	13.9
CYSCLM	1.5	-6.8	-6.0	-3.2	-2.0	-3.4
RMSE		**5.8**	**5.6**	**4.2**	**4.0**	**5.1**

Table S8: Experimental and predicted values for the 35 chemical shifts (ppm) in the ^{15}N benchmark dataset, as computed with GIPAW PBE and after monomer-correction with various functionals. The crystal structures were optimized with PBE0-D3(BJ).

^{15}N Chemical Shifts (ppm) using PBE0-D3(BJ) Structures

RefCode	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
BITZAF	249.5	244.6	244.8	247.8	248.8	245.6
GEHHEH	187.4	171.5	175.6	174.3	176.8	179.2
	261.0	256.1	257.1	259.9	260.9	259.5
GEHHIL	268.5	270.0	269.4	270.3	270.0	264.9
	261.2	264.5	262.5	265.8	265.6	264.3
LHISTD02	210.8	212.0	212.2	212.5	212.6	213.2
	132.6	135.1	136.4	135.3	136.2	138.1
LHISTD13	210.6	211.4	211.6	211.9	212.0	212.7
	132.4	136.4	137.8	136.6	137.5	139.4
TEJWAG	143.9	144.5	145.8	145.0	145.7	147.6
GLYCIN03	-6.5	-12.2	-12.0	-8.5	-7.5	-9.0
FUSVAQ01	183.2	182.7	181.4	180.8	180.1	183.0
	174.2	172.0	171.8	170.9	170.6	173.1
	192.2	191.1	190.3	191.6	191.1	188.7
	120.2	125.4	126.1	123.7	124.1	126.5
	50.2	48.8	49.3	50.0	50.5	48.9
CYTSIN	110.2	113.3	113.8	110.9	110.3	111.7
	165.2	165.4	164.6	161.5	160.2	163.1
	54.2	50.6	50.6	52.6	53.3	51.8
THYMIN01	90.2	94.2	94.4	91.4	90.1	89.9
	119.2	120.3	120.0	116.9	116.0	117.6
URACIL	96.2	103.3	103.2	100.3	98.8	98.7
	120.2	120.9	120.2	117.2	116.2	117.6
CIMETD	130.5	134.4	135.4	134.0	134.8	137.1
	213.1	213.0	213.2	213.2	213.2	213.7
	56.6	56.7	56.1	57.3	57.3	56.8
	43.5	42.1	40.3	43.3	43.1	41.8
	45.8	41.9	41.0	42.7	42.1	39.9
	149.9	146.1	144.9	147.7	147.2	141.4
BAPLOT01	114.7	121.3	119.0	116.9	115.0	116.4
	72.7	78.1	76.1	75.4	73.6	72.5
	122.7	126.4	128.1	127.0	128.0	129.9
	178.7	180.2	179.1	179.9	179.5	180.4
LTYRHC10	8.0	4.4	5.3	7.1	8.2	7.6
CYSCLM	1.5	-1.9	-1.0	1.3	2.4	1.2
RMSE		**4.3**	**4.0**	**3.3**	**3.2**	3.8

S2 Impact of variable unit cell crystal structure optimizations

The main results presented in this study employ crystal structures that were optimized with the lattice parameters constrained to their experimental values. This ensures that the optimizations effectively account for finite-temperature thermal expansion and leads to more accurate chemical shifts relative to experiment.[1] However, one might question whether constraining the lattice parameters artificially reduces the differences between the PBE-D3(BJ) and PBE0-D3(BJ) structures. This question is particularly relevant NMR crystallography problems where the experimental lattice parameters are not known *a priori*. Here, we investigate the impact of variable-cell crystal structure optimizations on the ^{15}N dataset chemical shifts.

Table S9 summarizes the root-mean-square errors for obtained with both fixed-cell and variable-cell geometry optimizations. For both the PBE-D3(BJ) and PBE0-D3(BJ) geometry optimizations, using the variable-cell optimizations increases the rms errors by 0.8–0.9 ppm. However, this change in the statistical errors is quite uniform and does not substantially alter the relative accuracy of the chemical shifts between the GGA and hybrid functional structures. The detailed variable-cell results underlying Table S9 are provided in the following sections.

Table S9: Summary of the root-mean-square chemical shift errors (ppm) for the ^{15}N test set using either fixed experimental lattice parameters or fully-optimized unit cells. The change in rms error due to allowing the unit cell parameters to relax is also indicated.

Geometry	Lattice Parameters	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
PBE-D3(BJ)	Fixed	5.8	5.6	4.2	4.0	5.1
PBE-D3(BJ)	Variable	6.6	6.6	5.0	4.6	5.9
Change: Fixed → Variable		**+0.8**	**+1.0**	**+0.8**	**+0.6**	**+0.7**
PBE0-D3(BJ)	Fixed	4.3	4.0	3.3	3.2	3.8
PBE0-D3(BJ)	Variable	5.1	5.1	4.2	4.1	4.7
Change: Fixed → Variable		**+0.8**	**+1.1**	**+0.9**	**+1.0**	**+0.8**

S2.1 Comparison of variable-cell DFT and experimental crystal structures

Table S10 lists the rmsd15 errors for the variable-cell DFT-optimized crystal structures relative to the experimental ones. Hydrogen atoms were excluded from the rmsd15 comparison.

Table S10: The rmsd15 errors (Å) computed from overlays of the DFT-optimized and experimental crystal structures in the ^{15}N test set (variable cell optimizations).

RefCode	PBE-D3(BJ) Structures	PBE0-D3(BJ) Structures
BAPLOT01	0.262	0.268
BITZAF	0.209	0.236
CIMETD	0.310	0.334
CYSCLM11	0.242	0.242
CYTSIN	0.180	0.196
FUSVAQ01	0.161	0.166
GEHHEH	0.460	0.410
GEHHIL	0.635	0.494
GLYCIN03	0.257	0.254
LHISTD02	0.261	0.284
LHISTD13	0.240	0.262
LTYRHC10	0.233	0.273
TEJWAG	0.170	0.190
THYMIN01	1.156	1.119
URACIL	0.169	0.193
Mean	**0.330**	**0.328**

Note: The variable-cell THYMIN01 structure changed significantly in the CRYSTAL17 geometry optimizations. The reason for this behavior is unclear, and it did not occur in any fixed-cell optimizations or in a variable-cell planewave DFT optimization of THYMIN01. Nevertheless, the errors in the chemical shifts remain within acceptable agreement of experiment (Tables S12 and S13) despite the structural changes. Since the variable cell structure optimizations are not the primary focus of the paper, this issue was not investigated further.

S2.2 Nitrogen variable-cell predicted shifts

Tables S12 and S13 show the resulting experimental and predicted shifts as for the ^{15}N data set computed with the PBE-D3(BJ) and PBE0-D3(BJ) variable unit cell structure optimizations, respectively. Table S11 lists the linear regression parameters that were fitted to map the computed absolute chemical shieldings to the chemical shifts listed in Tables S12 and S13.

Table S11: ^{15}N linear regression parameters for structures optimized with variable unit cell parameters

Structure Optimization	Chemical Shieldings	Slope	Intercept (ppm)
PBE-D3(BJ)	GIPAW PBE	-0.9615	176.03
	GIPAW + ΔPBE0	-1.0162	186.24
PBE0-D3(BJ)	GIPAW PBE	-0.9733	183.08
	GIPAW + ΔPBE0	-1.0239	193.03

Table S12: Experimental and predicted values for the 35 chemical shifts (ppm) in the ^{15}N benchmark dataset, as computed with GIPAW PBE and after monomer-correction with PBE0. Both the atomic positions and lattice parameters were optimized with PBE-D3(BJ) for these structures.

PBE-D3(BJ) Variable Cell Structures

RefCode	^{15}N Expt. Shift	GIPAW PBE	GIPAW +ΔPBE0
BITZAF	249.5	241.1	244.3
GEHHEH	187.4	173.2	175.7
	261.0	248.8	254.1
GEHHIL	268.5	269.1	269.9
	261.2	258.1	259.7
LHISTD02	210.8	214.1	214.5
	132.6	136.6	136.7
LHISTD13	210.6	213.9	214.3
	132.4	137.5	137.5
TEJWAG	143.9	144.5	145.0
GLYCIN03	-6.5	-20.1	-15.8
FUSVAQ01	183.2	180.8	179.0
	174.2	171.0	169.8
	192.2	190.9	191.5
	120.2	130.5	128.5
	50.2	50.9	52.0
CYTSIN	110.2	116.4	113.7
	165.2	163.5	159.4
	54.2	50.4	52.5
THYMIN01	90.2	97.3	94.3
	119.2	122.8	119.3
URACIL	96.2	107.9	104.6
	120.2	121.0	117.2
CIMETD	130.5	139.3	138.6
	213.1	214.1	214.3
	56.6	57.2	57.9
	43.5	42.3	43.7
	45.8	39.5	40.4
	149.9	149.3	150.8
BAPLOT01	114.7	123.9	119.0
	72.7	78.7	76.1
	122.7	129.8	130.0
	178.7	178.9	178.3
LTYRHC10	8.0	-1.7	1.5
CYSCLM	1.5	-7.2	-3.4
RMSE		**6.6**	**5.0**

Table S13: Experimental and predicted values for the 35 chemical shifts (ppm) in the ^{15}N benchmark dataset, as computed with GIPAW PBE and after monomer-correction with PBE0. Both the atomic positions and lattice parameters were optimized with PBE0-D3(BJ) for these structures.

PBE0-D3(BJ) Variable Cell Structures

RefCode	^{15}N Expt. Shift	GIPAW PBE	GIPAW +ΔPBE0
BITZAF	249.5	243.7	246.7
GEHHEH	187.4	172.0	174.5
	261.0	258.0	262.2
GEHHIL	268.5	268.4	268.9
	261.2	262.3	263.7
LHISTD02	210.8	212.3	212.8
	132.6	136.0	136.2
LHISTD13	210.6	212.3	212.9
	132.4	136.8	136.9
TEJWAG	143.9	143.5	144.1
GLYCIN03	-6.5	-15.8	-12.0
FUSVAQ01	183.2	179.0	177.1
	174.2	170.0	169.0
	192.2	189.8	190.4
	120.2	129.0	127.2
	50.2	50.7	51.8
CYTSIN	110.2	113.7	111.2
	165.2	162.9	159.1
	54.2	52.5	54.4
THYMIN01	90.2	96.0	93.2
	119.2	121.7	118.1
URACIL	96.2	105.7	102.6
	120.2	120.1	116.3
CIMETD	130.5	138.5	138.0
	213.1	212.9	213.2
	56.6	56.0	56.6
	43.5	42.2	43.5
	45.8	40.9	41.7
	149.9	150.3	151.8
BAPLOT01	114.7	121.4	116.8
	72.7	77.2	74.5
	122.7	127.7	128.1
	178.7	178.8	178.3
LTYRHC10	8.0	2.1	5.0
CYSCLM	1.5	-4.0	-0.5
RMSE		**5.1**	**4.2**

S3 NMR crystallography case studies

The chemical shifts for all carbon and nitrogen sets for the testosterone, acetaminophen, and phenobarbital crystalline structures are listed below. For phenobarbital, only ^{15}N chemical shifts are discussed in the main paper, but the ^{13}C chemical shifts are included here for completeness. The molecule naming and atomic numbering schemes used for these crystals can be found in ref 3.

S3.1 Testosterone

Table S14: Experimental and predicted ^{13}C chemical shifts for α and β testosterone, using crystal structures optimized with PBE-D3(BJ).

Testosterone Chemical Shifts (ppm) using PBE-D3(BJ) Structures

^{13}C Chemical shifts for all polymorphic forms of testosterone optimized with PBE-D3(BJ)						
Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
			α-Testosterone ($Z' = 2$): Molecule u			
C1	36.2	34.2	35.7	36.0	36.5	35.7
C2	34.6	30.7	31.6	33.2	33.6	31.8
C3	201.2	206.4	204.8	204.8	203.6	203.2
C4	125.7	124.9	123.8	123.8	123.7	124.2
C5	170.6	180.9	180.4	178.3	176.1	173.4
C6	33.8	32.5	34.1	34.1	34.2	32.5
C7	32.4	31.7	32.9	33.3	33.7	32.7
C8	36.9	33.5	34.5	34.6	34.8	34.2
C9	54.1	54.1	53.7	52.9	52.5	53.1
C10	40.0	39.8	40.1	40.5	40.2	39.2
C11	23.0	17.9	19.7	21.1	21.8	19.9
C12	36.8	35.0	36.8	36.6	36.9	36.0
C13	43.7	41.0	39.9	42.2	42.4	41.7
C14	51.1	50.2	50.3	50.2	50.2	50.4
C15	24.3	21.0	23.0	24.2	24.9	23.0
C16	30.2	25.5	26.8	27.9	28.4	26.8
C17	80.4	86.0	85.6	83.0	82.1	83.6
C18	11.7	6.2	9.7	11.7	13.2	10.6
C19	18.6	10.8	13.4	15.5	16.8	14.5
			α-Testosterone ($Z' = 2$): Molecule v			
C1	37.2	33.7	35.1	35.5	35.9	35.0
C2	33.8	33.0	33.9	35.3	35.5	33.8
C3	202.7	206.1	204.5	204.4	203.2	202.7
C4	125.2	124.0	122.9	122.9	122.7	123.2
C5	172.1	181.5	181.1	178.9	176.7	174.0
C6	33.5	33.2	34.7	34.7	34.8	33.0
C7	32.3	30.7	31.9	32.2	32.6	31.5
C8	36.4	34.5	35.3	35.6	35.8	35.2
C9	55.3	53.1	52.8	52.2	51.8	52.2
C10	39.6	40.1	40.2	40.7	40.5	39.5
C11	22.0	19.6	21.5	22.6	23.2	21.3
C12	38.4	33.5	35.3	35.3	35.6	34.5
C13	43.6	41.4	40.0	42.4	42.6	41.8
C14	51.9	49.6	49.8	49.6	49.4	49.4
C15	24.2	21.0	23.0	24.3	25.1	23.1
C16	29.9	26.6	28.2	29.5	30.3	28.7
C17	82.7	82.6	82.2	79.8	79.0	80.3
C18	12.2	5.6	9.0	11.1	12.6	9.8
C19	17.9	15.3	17.9	19.7	21.0	18.9
			β-Testosterone			

Continued on next page

Testosterone Chemical Shifts (ppm) using PBE-D3(BJ) Structures *(continued)*

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
C1	35.3	32.8	34.3	34.7	35.2	34.4
C2	35.3	32.5	33.5	34.9	35.3	33.7
C3	200.2	204.2	202.5	202.7	201.6	201.0
C4	124.7	125.4	124.3	124.3	124.1	124.6
C5	173.8	185.1	184.7	182.2	180.2	177.6
C6	33.5	32.8	34.4	34.4	34.5	32.7
C7	33.5	32.9	34.1	34.1	34.4	33.3
C8	35.3	32.8	33.7	33.9	34.1	33.4
C9	54.7	54.4	53.9	53.2	52.8	53.3
C10	39.4	40.0	40.2	40.6	40.4	39.3
C11	21.0	17.5	19.4	20.6	21.3	19.3
C12	35.3	33.3	35.2	35.2	35.6	34.5
C13	43.6	42.0	40.7	43.0	43.2	42.6
C14	51.6	50.4	50.6	50.3	50.3	50.5
C15	24.0	21.0	23.1	24.3	25.0	23.1
C16	28.8	25.5	27.1	28.4	29.0	27.2
C17	80.7	84.0	83.7	81.2	80.4	81.8
C18	12.6	6.9	10.4	12.4	13.9	11.2
C19	16.9	12.0	14.8	16.7	18.0	15.7
^{13}C RMSE		**3.9**	**3.1**	**2.3**	**1.9**	**1.8**

Table S15: Experimental and predicted ^{13}C chemical shifts for α and β testosterone, using crystal structures optimized with PBE0-D3(BJ).

Testosterone Chemical Shifts (ppm) using PBE0-D3(BJ) Structures

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
			α-Testosterone ($Z' = 2$): Molecule u			
C1	36.2	35.2	36.7	36.9	37.3	36.6
C2	34.6	31.7	32.4	33.9	34.3	32.6
C3	201.2	205.8	204.1	204.0	202.9	202.4
C4	125.7	126.1	125.0	125.0	124.8	125.3
C5	170.6	180.9	180.4	178.3	176.2	173.7
C6	33.8	33.4	34.9	34.8	34.9	33.3
C7	32.4	32.5	33.6	33.8	34.2	33.3
C8	36.9	34.1	35.0	35.1	35.2	34.6
C9	54.1	54.8	54.5	53.6	53.2	53.8
C10	40.0	39.6	39.8	40.2	39.9	38.9
C11	23.0	18.5	20.3	21.5	22.2	20.4
C12	36.8	36.0	37.8	37.4	37.7	36.8
C13	43.7	41.0	39.8	42.1	42.3	41.7
C14	51.1	51.1	51.2	50.9	50.9	51.2
C15	24.3	21.4	23.3	24.4	25.1	23.3
C16	30.2	26.3	27.5	28.5	29.0	27.5
C17	80.4	85.8	85.4	83.0	82.1	83.6
C18	11.7	7.1	10.5	12.3	13.8	11.3
C19	18.6	11.7	14.3	16.2	17.5	15.3
			α-Testosterone ($Z' = 2$): Molecule v			
C1	37.2	34.8	36.2	36.4	36.7	35.9
C2	33.8	33.6	34.4	35.7	35.9	34.3
C3	202.7	205.8	204.2	204.0	202.8	202.3
C4	125.2	125.2	124.0	124.1	123.9	124.3
C5	172.1	181.8	181.3	179.1	177.0	174.5
C6	33.5	34.2	35.6	35.4	35.5	33.9
C7	32.3	31.4	32.6	32.8	33.2	32.2
C8	36.4	35.0	35.9	36.0	36.2	35.7
C9	55.3	54.0	53.7	52.9	52.5	53.0
C10	39.6	39.8	37.5	40.4	40.1	39.1

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Testosterone Chemical Shifts (ppm) using PBE0-D3(BJ) Structures ***(continued)***

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
C11	22.0	20.1	21.9	22.9	23.5	21.7
C12	38.4	34.6	36.4	36.1	36.4	35.4
C13	43.6	41.4	40.0	42.4	42.5	41.8
C14	51.9	50.5	50.7	50.3	50.1	50.2
C15	24.2	21.4	23.3	24.5	25.3	23.5
C16	29.9	27.5	29.1	30.3	31.0	29.5
C17	82.7	82.5	82.2	79.8	79.1	80.3
C18	12.2	6.6	9.9	11.8	13.2	10.7
C19	17.9	16.1	18.7	20.3	21.6	19.6
			β-Testosterone			
C1	35.3	33.9	35.3	35.6	36.0	35.3
C2	35.3	33.2	34.1	35.4	35.8	34.3
C3	200.2	203.9	202.2	202.3	201.2	200.7
C4	124.7	126.5	125.3	125.4	125.1	125.6
C5	173.8	185.0	184.6	182.1	180.1	177.7
C6	33.5	33.7	35.3	35.1	35.1	33.5
C7	33.5	33.6	34.7	34.7	35.0	34.0
C8	35.3	33.4	34.4	34.4	34.6	33.9
C9	54.7	54.9	54.5	53.6	53.2	53.9
C10	39.4	39.8	39.9	40.3	40.1	39.0
C11	21.0	18.0	19.8	20.9	21.6	19.7
C12	35.3	34.4	36.2	36.0	36.3	35.4
C13	43.6	42.0	40.6	42.9	43.1	42.5
C14	51.6	51.1	51.4	50.9	50.9	51.1
C15	24.0	21.4	23.5	24.5	25.2	23.4
C16	28.8	26.0	27.6	28.7	29.3	27.6
C17	80.7	83.9	83.6	81.2	80.4	81.7
C18	12.6	7.7	11.0	12.9	14.3	11.8
C19	16.9	12.9	15.6	17.3	18.6	16.5
^{13}C RMSE		**3.5**	**2.9**	**2.2**	**1.9**	**1.5**

S3.2 Acetaminophen

Table S16: Experimental and predicted ^{13}C and ^{15}N chemical shifts (ppm) for three polymorphs of acetaminophen, using crystal structures optimized with PBE-D3(BJ).

Acetaminophen Chemical Shifts (ppm) using PBE-D3(BJ) Structures

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
			Form I			
C1	132.6	131.2	131.2	131.5	131.8	132.4
C2	123.1	121.7	121.5	123.1	123.5	122.5
C3	115.3	113.5	112.8	115.3	116.0	114.9
C4	152.0	153.4	152.5	151.4	151.1	152.5
C5	116.1	115.8	115.1	117.0	117.5	116.7
C6	120.3	117.6	117.1	118.9	119.2	118.0
C7	169.4	168.3	168.5	170.3	170.7	170.3
C8	23.5	19.2	21.1	24.0	25.3	22.9
N1	97.9	101.7	102.0	98.3	97.0	97.1
			Form II			
C1	131.6	130.3	130.3	130.6	130.9	131.6
C2	120.2	119.1	119.1	120.7	121.2	119.9
C3	117.1	115.9	115.4	117.7	118.3	117.3
C4	153.2	155.0	154.3	153.1	152.8	154.3
C5	118.4	116.7	116.2	117.8	118.4	117.7
C6	120.2	118.8	118.4	120.0	120.3	119.1
C7	170.6	169.1	169.3	171.0	171.4	170.9
C8	25.1	20.9	22.7	25.7	27.1	24.7
N1	98.3	104.3	104.8	101.0	99.6	100.1
			Form III ($Z' = 2$)			
C1	131.1	129.2	129.0	129.5	129.8	130.4
C2	124.8	124.2	123.7	125.5	126.0	124.9
C3	118.3	116.7	116.1	118.4	119.0	118.1
C4	151.9	153.1	152.2	151.3	150.8	152.2
C5	118.3	116.9	116.2	117.9	118.3	117.6
C6	123.2	122.0	121.5	123.2	123.6	122.4
C7	170.0	168.9	169.0	170.9	171.2	170.5
C8	24.3	19.2	21.2	24.1	25.5	23.0
N1	96.3	98.2	98.1	94.7	93.5	93.5
C1'	131.1	129.6	129.4	130.0	130.3	131.1
C2'	124.8	121.4	121.0	122.8	123.2	122.0
C3'	118.3	116.5	115.9	118.1	118.7	117.7
C4'	151.9	153.4	152.5	151.5	151.0	152.3
C5'	118.3	117.5	116.9	118.6	119.0	118.3
C6'	123.2	120.6	120.0	121.7	122.1	121.1
C7'	170.0	168.4	168.5	170.4	170.8	170.0
C8'	24.3	19.3	21.2	24.1	25.4	23.0
N1'	95.0	97.6	97.5	94.3	92.9	92.8
^{13}C RMSE		**2.2**	**2.0**	**0.8**	**1.1**	**1.0**
^{15}N RMSE		**3.9**	**4.1**	**1.6**	**1.9**	**2.0**

Table S17: Experimental and predicted ^{13}C and ^{15}N chemical shifts (ppm) for three polymorphs of acetaminophen, using crystal structures optimized with PBE0-D3(BJ).

Acetaminophen Chemical Shifts (ppm) using PBE0-D3(BJ) Structures

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
			Form I			
C1	132.6	131.6	131.5	131.9	132.2	132.7
C2	123.1	123.2	122.9	124.6	125.0	123.9
C3	115.3	114.6	113.9	116.3	117.0	115.9
C4	152.0	153.7	152.8	151.9	151.7	153.0
C5	116.1	116.9	116.2	118.0	118.5	117.7
C6	120.3	119.0	118.3	120.2	120.5	119.3
C7	169.4	167.5	167.5	169.3	169.7	169.4
C8	23.5	19.2	20.9	23.8	25.2	22.8
N1	97.9	100.8	101.0	97.6	96.2	96.3
			Form II			
C1	131.6	130.8	130.7	131.1	131.3	131.8
C2	120.2	120.6	120.3	122.1	122.5	121.2
C3	117.1	116.9	116.3	118.4	119.0	118.1
C4	153.2	155.3	154.5	153.5	153.2	154.6
C5	118.4	117.8	117.1	118.9	119.3	118.6
C6	120.2	120.3	119.7	121.5	121.8	120.6
C7	170.6	168.6	168.7	170.3	170.6	170.3
C8	25.1	21.6	23.4	26.1	27.4	25.1
N1	98.3	101.7	101.9	98.5	97.3	97.5
			Form III ($Z' = 2$)			
C1	131.1	130.0	129.8	130.3	130.6	131.1
C2	124.8	125.3	124.8	126.6	127.0	126.0
C3	118.3	118.0	117.3	119.5	120.1	119.2
C4	151.9	153.7	152.8	152.0	151.5	152.9
C5	118.3	118.0	117.2	118.9	119.3	118.6
C6	123.2	123.3	122.7	124.4	124.8	123.6
C7	170.0	168.3	168.4	170.1	170.4	170.0
C8	24.3	20.2	22.0	24.8	26.2	23.8
N1	96.3	98.1	97.9	94.7	93.5	93.5
C1'	131.1	130.3	130.1	130.7	131.0	131.7
C2'	124.8	122.5	122.1	123.9	124.3	123.1
C3'	118.3	117.4	116.8	119.0	119.5	118.5
C4'	151.9	154.0	153.0	152.1	151.7	153.0
C5'	118.3	118.4	117.7	119.5	119.8	119.1
C6'	123.2	121.9	121.2	123.0	123.3	122.3
C7'	170.0	168.0	168.0	169.8	170.2	169.6
C8'	24.3	20.1	21.9	24.7	26.0	23.8
N1'	95.0	97.5	97.4	94.3	93.0	92.8
^{13}C RMSE		**1.8**	**1.4**	**0.9**	**1.3**	**0.8**
^{15}N RMSE		**2.7**	**2.8**	**0.9**	**2.0**	**2.0**

S3.3 Phenobarbital

Table S18: Experimental and predicted ^{13}C and ^{15}N chemical shifts (ppm) for two polymorphs of phenobarbital, using crystal structures optimized with PBE-D3(BJ).

Phenobarbital Chemical Shifts (ppm) using PBE-D3(BJ) Structures

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
			Form II ($Z' = 3$): Molecule A			
C1	147.2	146.3	146.5	147.2	147.7	147.8
C2	136.0	138.2	137.2	136.3	135.6	136.2
C3	61.7	63.3	64.6	62.8	62.1	61.5
C4	30.4	31.9	32.7	33.2	33.3	31.8
C5	6.9	1.6	3.9	7.0	8.4	5.5
C6	177.4	177.7	177.6	177.2	176.6	175.9
C7	177.4	180.0	180.1	179.6	179.2	178.9
C8	125.8	128.7	128.5	128.9	128.9	127.7
C9	131.4	130.7	129.6	130.9	131.0	130.5
C10	132.4	131.5	130.7	132.1	132.3	131.5
C11	132.8	130.2	129.2	130.5	130.7	130.2
C12	129.7	126.4	126.0	127.3	127.5	126.3
N	116.1	125.0	124.6	120.5	119.2	120.6
N	111.5	117.6	117.1	114.0	112.8	113.8
			Form II ($Z' = 3$): Molecule B			
C1	148.9	147.7	148.1	148.8	149.4	149.5
C2	137.2	139.5	138.4	137.4	136.7	137.3
C3	61.0	62.1	63.4	61.6	61.0	60.5
C4	32.2	33.0	33.9	34.4	34.5	33.1
C5	7.9	2.6	4.8	8.0	9.4	6.5
C6	169.9	172.4	172.3	171.8	171.2	170.5
C7	173.2	174.5	174.5	174.3	173.9	173.6
C8	127.0	126.3	126.1	126.8	126.9	125.7
C9	130.2	129.7	128.6	129.9	130.0	129.4
C10	129.3	128.6	127.7	129.3	129.6	128.5
C11	127.0	125.7	124.6	126.3	126.5	125.7
C12	127.0	127.0	126.7	128.0	128.1	126.8
N	113.9	122.0	121.2	117.6	116.3	117.5
N	108.3	114.0	113.1	110.4	109.2	110.0
			Form II ($Z' = 3$): Molecule C			
C1	147.2	146.1	146.4	147.0	147.5	147.6
C2	137.2	139.0	137.9	137.0	136.5	137.4
C3	62.4	63.1	64.2	62.3	61.6	60.9
C4	27.2	26.3	27.5	28.4	28.8	27.2
C5	8.9	2.8	5.0	8.2	9.6	6.7
C6	173.2	176.6	176.4	176.2	175.8	175.5
C7	175.0	175.7	175.7	175.3	174.7	174.0
C8	125.4	124.7	124.4	125.9	126.2	124.7
C9	133.7	130.8	129.8	131.0	131.2	130.7
C10	130.2	130.7	129.9	131.3	131.5	130.5
C11	130.2	133.7	132.7	133.6	133.7	133.3
C12	125.8	123.8	123.7	124.6	124.7	123.3
N	115.2	124.5	124.3	120.4	119.1	120.4
N	109.8	115.7	114.6	111.7	110.3	111.3
			Form III			
C1	149.0	147.6	147.9	148.6	149.1	149.2
C2	137.6	139.2	137.9	137.1	136.5	137.3
C3	62.3	63.9	64.9	62.9	62.2	61.6
C4	27.1	25.6	26.8	28.0	28.4	26.8
C5	11.4	6.7	9.0	11.9	13.3	10.6
C6	174.2	177.5	177.6	177.0	176.4	175.6
C7	174.2	175.2	175.2	175.0	174.7	174.3

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Phenobarbital Chemical Shifts (ppm) using PBE-D3(BJ) Structures *(continued)*

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
C8	127.6	126.9	126.8	127.5	127.6	126.5
C9	130.7	130.1	129.0	130.2	130.3	129.7
C10	129.5	128.6	127.8	129.4	129.6	128.6
C11	129.9	129.4	128.4	129.8	130.0	129.5
C12	127.6	126.9	126.7	128.0	128.2	127.0
N	114.5	120.7	120.2	116.7	115.3	116.4
N	108.6	114.8	113.7	110.9	109.5	110.4
^{13}C RMSE		**2.3**	**2.1**	**1.4**	**1.4**	**1.4**
^{15}N RMSE		**7.2**	**6.6**	**3.2**	**2.1**	**3.1**

Table S19: Experimental and predicted ^{13}C and ^{15}N chemical shifts (ppm) for two polymorphs of phenobarbital, using crystal structures optimized with PBE0-D3(BJ).

Phenobarbital Chemical Shifts (ppm) using PBE0-D3(BJ) Structures

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
Form II ($Z' = 3$): Molecule A						
C1	147.2	146.5	146.6	147.4	147.9	148.1
C2	136.0	139.4	138.5	137.5	136.8	137.4
C3	61.7	63.2	64.6	62.7	61.9	61.4
C4	30.4	32.9	33.6	34.0	34.0	32.6
C5	6.9	2.1	4.3	7.3	8.7	5.9
C6	177.4	177.2	177.0	176.6	176.0	175.5
C7	177.4	179.8	179.8	179.3	178.9	178.8
C8	125.8	129.8	129.5	130.0	130.0	128.7
C9	131.4	131.6	130.5	131.8	131.9	131.4
C10	132.4	132.6	131.7	133.1	133.3	132.5
C11	132.8	131.0	130.0	131.3	131.5	130.9
C12	129.7	127.7	127.3	128.6	128.7	127.5
N	116.1	123.9	123.5	119.7	118.5	119.8
N	111.5	117.2	116.7	113.8	112.7	113.7
Form II ($Z' = 3$): Molecule B						
C1	148.9	147.9	148.1	148.9	149.5	149.7
C2	137.2	140.8	139.7	138.8	138.0	138.6
C3	61.0	62.1	63.4	61.5	60.9	60.3
C4	32.2	33.7	34.6	35.0	35.1	33.8
C5	7.9	3.3	5.5	8.5	9.9	7.2
C6	169.9	172.6	172.4	171.9	171.4	170.8
C7	173.2	174.5	174.5	174.2	173.9	173.7
C8	127.0	127.6	127.3	128.0	128.0	126.8
C9	130.2	126.8	125.6	127.2	127.3	126.5
C10	129.3	129.6	128.6	130.3	130.5	129.5
C11	127.0	130.7	129.6	131.0	131.1	130.5
C12	127.0	128.2	127.8	129.0	129.2	127.9
N	113.9	121.8	121.1	117.6	116.3	117.6
N	108.3	113.7	113.0	110.3	109.2	110.0
Form II ($Z' = 3$): Molecule C						
C1	147.2	146.3	146.4	147.2	147.7	147.8
C2	137.2	140.4	139.2	138.3	137.8	138.6
C3	62.4	63.2	64.3	62.3	61.6	60.9
C4	27.2	27.2	28.4	29.2	29.6	28.0
C5	8.9	3.5	5.7	8.7	10.1	7.4
C6	173.2	176.1	176.2	175.9	175.5	175.4
C7	175.0	175.5	175.5	175.1	174.5	174.0
C8	125.4	125.9	125.6	127.1	127.3	125.9
C9	133.7	131.7	130.7	132.0	132.1	131.5
C10	130.2	131.9	131.0	132.5	132.6	131.7

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Phenobarbital Chemical Shifts (ppm) using PBE0-D3(BJ) Structures *(continued)*

Atom	Expt. Shift	GIPAW PBE	GIPAW +ΔTPSS	GIPAW +ΔPBE0	GIPAW +ΔPBE0-DH	GIPAW +ΔDSD-PBEP86
C11	130.2	134.5	133.5	134.5	134.5	134.1
C12	125.8	125.0	124.9	125.7	125.8	124.5
N	115.2	123.4	122.9	119.2	117.9	119.2
N	109.8	115.0	114.5	111.7	110.5	111.2
			Form III			
C1	149.0	147.7	147.9	148.6	149.2	149.4
C2	137.6	140.4	139.1	138.3	137.7	138.5
C3	62.3	63.8	64.8	62.7	62.0	61.4
C4	27.1	26.5	27.7	28.6	29.0	27.5
C5	11.4	7.3	9.5	12.3	13.7	11.2
C6	174.2	177.0	177.2	176.6	176.0	175.4
C7	174.2	174.8	174.8	174.7	174.3	174.1
C8	127.6	127.9	127.7	128.4	128.5	127.4
C9	130.7	131.5	130.3	131.5	131.6	131.0
C10	129.5	129.7	128.7	130.4	130.6	129.7
C11	129.9	130.4	129.3	130.8	130.9	130.4
C12	127.6	127.9	127.6	128.9	129.1	127.9
N	114.5	119.9	119.3	116.0	114.7	115.8
N	108.6	114.3	113.7	110.8	109.6	110.4
^{13}C RMSE		**2.3**	**2.1**	**1.8**	**1.8**	**1.6**
^{15}N RMSE		**6.6**	**6.0**	**2.8**	**1.7**	**2.7**

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