Supplemental material for the publication: Electron correlation and relativistic effects in the secondary NMR isotope shifts of CSe_2

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Table I. Relativistic BPPT corrections to ^{77}Se and ^{13}C shielding constants, σ, in CSe_2 at equilibrium geometry.[a]

	σ_{Se}^{BPPT}				σ_{C}^{BPPT}			
Term	KT2	BLYP	B3LYP	BHandHLYP	KT2	BLYP	B3LYP	BHandHLYP
con	-161.65	-160.77	-160.69	-160.70	-0.78	-0.76	-0.75	-0.75
d-KE	-133.56	-132.83	-132.77	-132.77	-2.02	-1.99	-1.99	-1.99
p-OZ	-8.32	-8.29	-8.28	-8.27	-0.96	-0.95	-0.95	-0.95
d/MV	226.30	225.16	225.04	225.03	1.19	1.16	1.16	1.17
d/Dar	-123.47	-123.03	-123.00	-123.02	-0.77	-0.76	-0.77	-0.78
p/OZ-KE	33.29	33.54	33.49	33.39	2.27	2.27	2.28	2.29
p-KE/OZ	80.75	85.22	85.26	84.97	2.53	2.55	2.56	2.57
FC/SZKE	507.19	504.63	504.41	504.50	2.63	2.54	2.53	2.52
SD/SZKE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FC-II(1)	-87.12	-86.86	-86.83	-86.84	-0.34	-0.33	-0.32	-0.31
SD-II(1)	16.80	16.72	16.72	16.75	0.01	0.01	0.00	0.00
p/MV	-177.38	-184.52	-196.99	-213.32	-11.15	-12.34	-14.11	-16.99
p/DAR	24.53	24.51	32.35	43.02	5.42	6.19	7.37	9.27
FC-I(1)	29.62	30.91	36.55	43.99	43.91	45.98	47.59	50.81
SD-I(1)	-20.49	-22.30	-21.60	-19.77	-6.13	-6.90	-7.16	-7.61
FC-I(2)	-6.59	-6.93	-7.43	-8.06	-4.64	-4.85	-4.98	-5.28
SD-I(2)	0.10	0.17	0.12	-0.03	0.64	0.72	0.74	0.78
BPPT(1)	206.49	202.09	203.66	206.95	35.81	36.67	37.44	39.27
BPPT(1+2)[b]	200.00	195.34	196.35	198.87	31.81	32.54	33.19	34.77
BPPT-5[c]	-62.97	-66.18	-64.42	-61.12	34.58	35.48	36.25	38.06

[a] In ppm. For r_e(C-Se) = 1.6881 Å obtained at the CCSD(T)/cc-pV5Z level. All relativistic calculations at DFT level with FIVu6/HIVu6 basis set for Se/C. The common gauge origin was placed at the nucleus in question. [b] Both one- (1) and two-electron (2) third-order spin-orbit contributions (Ref. [1]) are included: SO-I(1+2)=FC-I(1)+SD-I(1)+FC-I(2)+SD-I(2). [c] BPPT-5 approximation with the numerically most important five terms, see Ref. [3].

Table II. Relativistic BPPT corrections to ^{77}Se and ^{13}C shielding anisotropies, $\Delta\sigma$, in CSe_2 at equilibrium geometry.[a]

	$\Delta\sigma_{Se}^{BPPT}$				$\Delta\sigma_{C}^{BPPT}$			
Term	KT2	BLYP	B3LYP	BHandHLYP	KT2	BLYP	B3LYP	BHandHLYP
dip	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
d-KE	0.55	0.55	0.55	0.55	2.14	2.13	2.13	2.13
p-OZ	0.36	0.36	0.36	0.36	1.43	1.42	1.42	1.42
d/MV	0.13	0.12	0.13	0.14	-0.47	-0.45	-0.47	-0.50
d/Dar	-0.06	-0.06	-0.06	-0.06	0.06	0.05	0.06	0.07
p/OZ-KE	-1.91	-2.01	-2.02	-2.01	-3.40	-3.41	-3.42	-3.45
p-KE/OZ	-121.12	-127.84	-127.88	-127.46	-3.80	-3.82	-3.84	-3.86
FC/SZKE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SD/SZKE	-0.09	-0.10	-0.10	-0.11	0.01	0.01	0.01	0.01
FC-II(1)	-0.20	-0.17	-0.20	-0.26	-0.11	-0.10	-0.11	-0.11
SD-II(1)	0.07	0.07	0.06	0.05	-0.01	0.00	0.00	-0.01
p/MV	266.07	276.79	295.48	319.99	16.73	18.50	21.16	25.48
p/DAR	-36.80	-36.77	-48.53	-64.52	-8.14	-9.28	-11.05	-13.91
FC-I(1)	-44.42	-46.37	-54.83	-65.98	-65.87	-68.97	-71.39	-76.22
SD-I(1)	53.15	55.38	53.51	49.95	6.48	7.30	7.95	8.96
FC-I(2)	9.89	10.39	11.14	12.08	6.96	7.27	7.48	7.92
SD-I(2)	-2.18	-2.23	-2.04	-1.72	-0.67	-0.75	-0.81	-0.90
BPPT(1)	115.73	119.96	116.47	110.62	-54.94	-56.63	-57.55	-59.98
BPPT(1+2)[b]	123.44	128.12	125.57	120.99	-48.65	-50.10	-50.88	-52.96
SOS[c]	-44.84	-43.86	-42.22	-40.58	5.43	6.10	5.59	4.92
BPPT(1)+SOS	70.89	76.10	74.25	70.04	-49.51	-50.53	-51.96	-55.06
BPPT(1+2)+SOS	78.60	84.26	83.34	80.41	-43.22	-44.00	-45.30	-48.04
BPPT-6[d]	72.03	77.33	75.52	71.39	-49.16	-50.17	-51.58	-54.63

[a] In ppm. For r_e(C-Se) = 1.6881 Å obtained at the CCSD(T)/cc-pV5Z level. Anisotropies with respect to the symmetry axis, $\Delta\sigma = \sigma_{||} - \sigma_{\perp}$. All relativistic calculations at DFT level with FIVu6/HIVu6 basis set for Se/C. A common gauge origin was placed at the nucleus in question. [b] Both one- (1) and two-electron (2) third-order spin-orbit contributions (Ref. [1]) are included: SO-I(1+2)=FC-I(1)+SD-I(1)+FC-I(2)+SD-I(2). [c] The SOS contribution, $\Delta\sigma^{SOS} = -3\sigma_{||}^{SD-I(1)}$, of Ref. [2] as appropriate to a linear molecule. [d] BPPT-6 approximation with the numerically most important six terms, see Ref. [3].

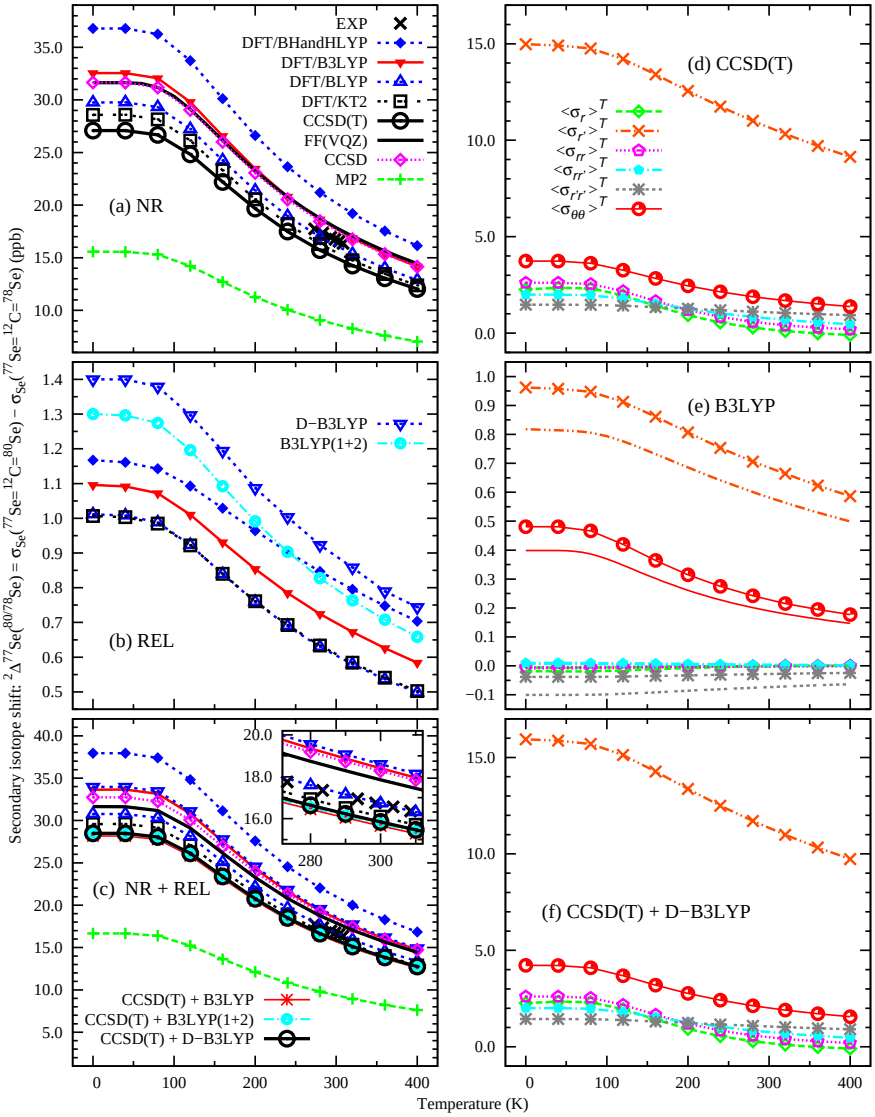

Figure 1. Electron correlation effects on the two-bond secondary ^{77}Se NMR isotope shift $^2\Delta^{77}\mathrm{Se}(^{80/78}\mathrm{Se}) = \sigma_{\mathrm{Se}}(^{77}\mathrm{Se}=^{12}\mathrm{C}=^{80}\mathrm{Se}) - \sigma_{\mathrm{Se}}(^{77}\mathrm{Se}=^{12}\mathrm{C}=^{78}\mathrm{Se})$ (the E–D splitting in Ref. [4]) at (a) the nonrelativistic (NR) level. (b) Relativistic corrections at the 4-component (D-B3LYP) as well as 1- and 2-electron [B3LYP(1+2)] BPPT levels of theory; with different DFT functionals. (c) The total results containing NR-data with MP2, CCSD, and CCSD(T), and the relativistic BPPT(1) contributions at the B3LYP level. The NR CCSD(T) result is also shown with BPPT corrections including both 1- and 2-electron spin-orbit contributions [B3LYP(1+2)]. Also NR+BPPT(1) results with different DFT functionals are displayed. Individual rovibrational contributions at CCSD(T)+D-B3LYP level for nonrelativistic/relativistic terms are displayed in panels (d)-(f), referencing to the terms in Eq. (2) in the article. In panel (e), the lines without symbols are B3LYP(1) results. FF(VQZ) denotes CCSD(T)+D-B3LYP results with the CCSD(T)/VQZ force field.

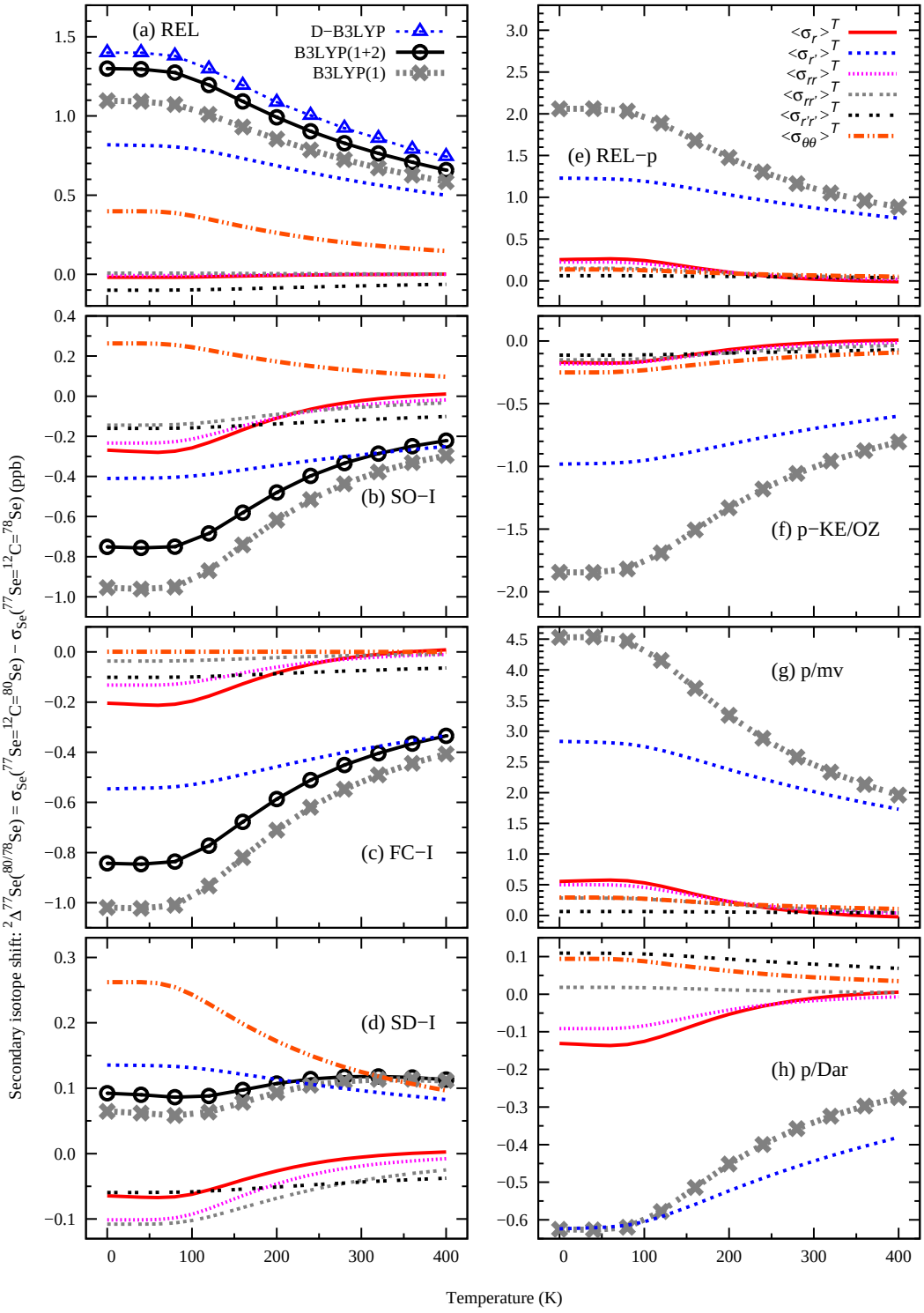

Figure 2. The temperature dependence of the main relativistic BPPT-5 contributions to the secondary ^{77}Se isotope shift $^2\Delta^{77}\mathrm{Se}(^{80/78}\mathrm{Se}) = \sigma_{\mathrm{Se}}(^{77}\mathrm{Se} = ^{12}\mathrm{C} = ^{80}\mathrm{Se}) - \sigma_{\mathrm{Se}}(^{77}\mathrm{Se} = ^{12}\mathrm{C} = ^{78}\mathrm{Se})$ (the E–D splitting in Ref. [4]). (a) The full BPPT effect. (b) Third-order spin-orbit (SO-I) contribution, a sum of (c) FC-I and (d) SD-I terms. (e) The scalar relativistic (REL-p) contribution, a sum of the relativistic paramagnetic terms in panels (f)-(h). Rovibrational contributions at B3LYP level are displayed in each panel.

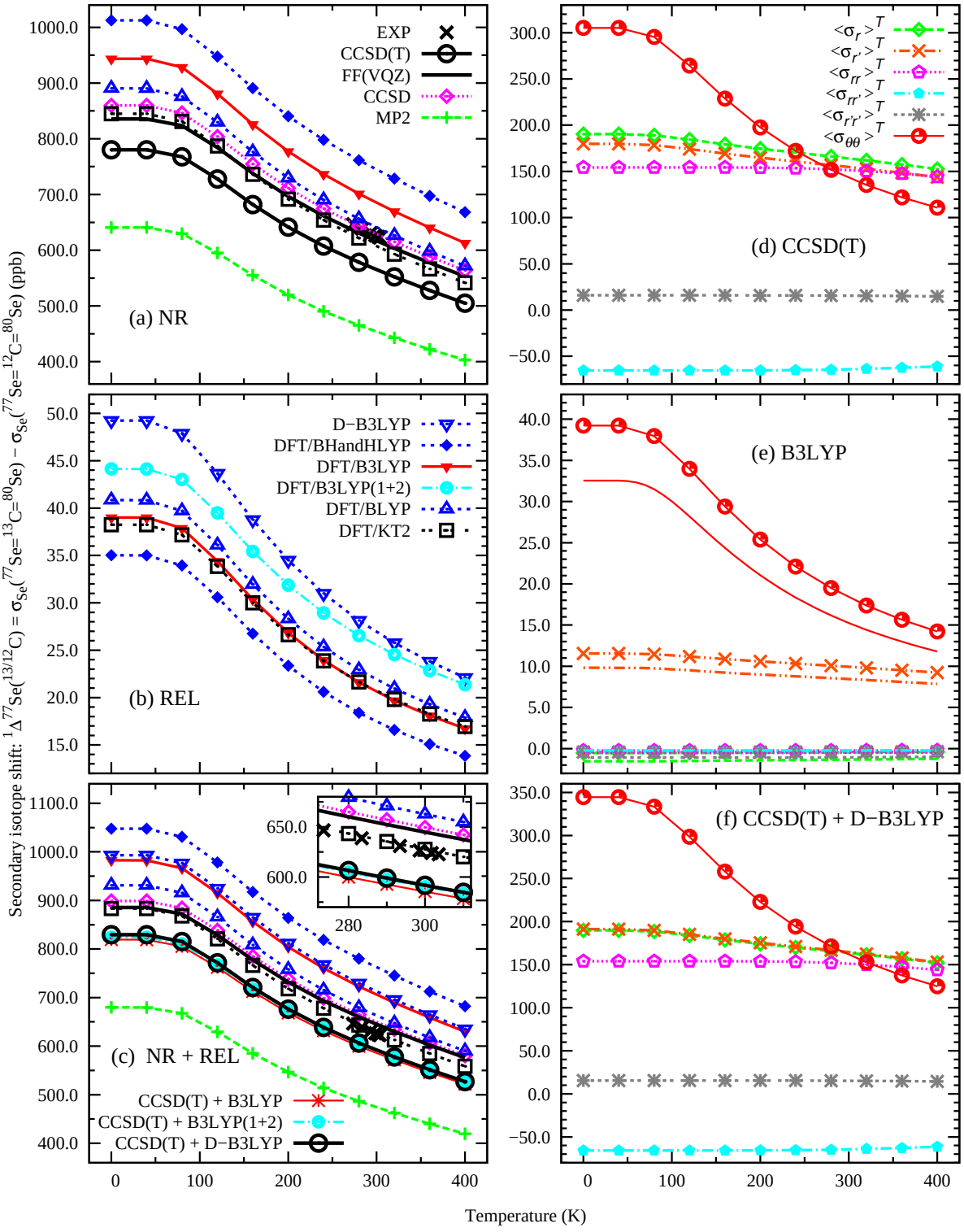

Figure 3. As in Fig. 1, but for the one-bond secondary ^{77}Se isotope shift: $^1\Delta^{77}\mathrm{Se}(^{13/12}\mathrm{C}) = \sigma_{\mathrm{Se}}(^{77}\mathrm{Se} = ^{13}\mathrm{C} = ^{80}\mathrm{Se}) - \sigma_{\mathrm{Se}}(^{77}\mathrm{Se} = ^{12}\mathrm{C} = ^{80}\mathrm{Se})$ (the E'-E splitting in Ref. [4]).

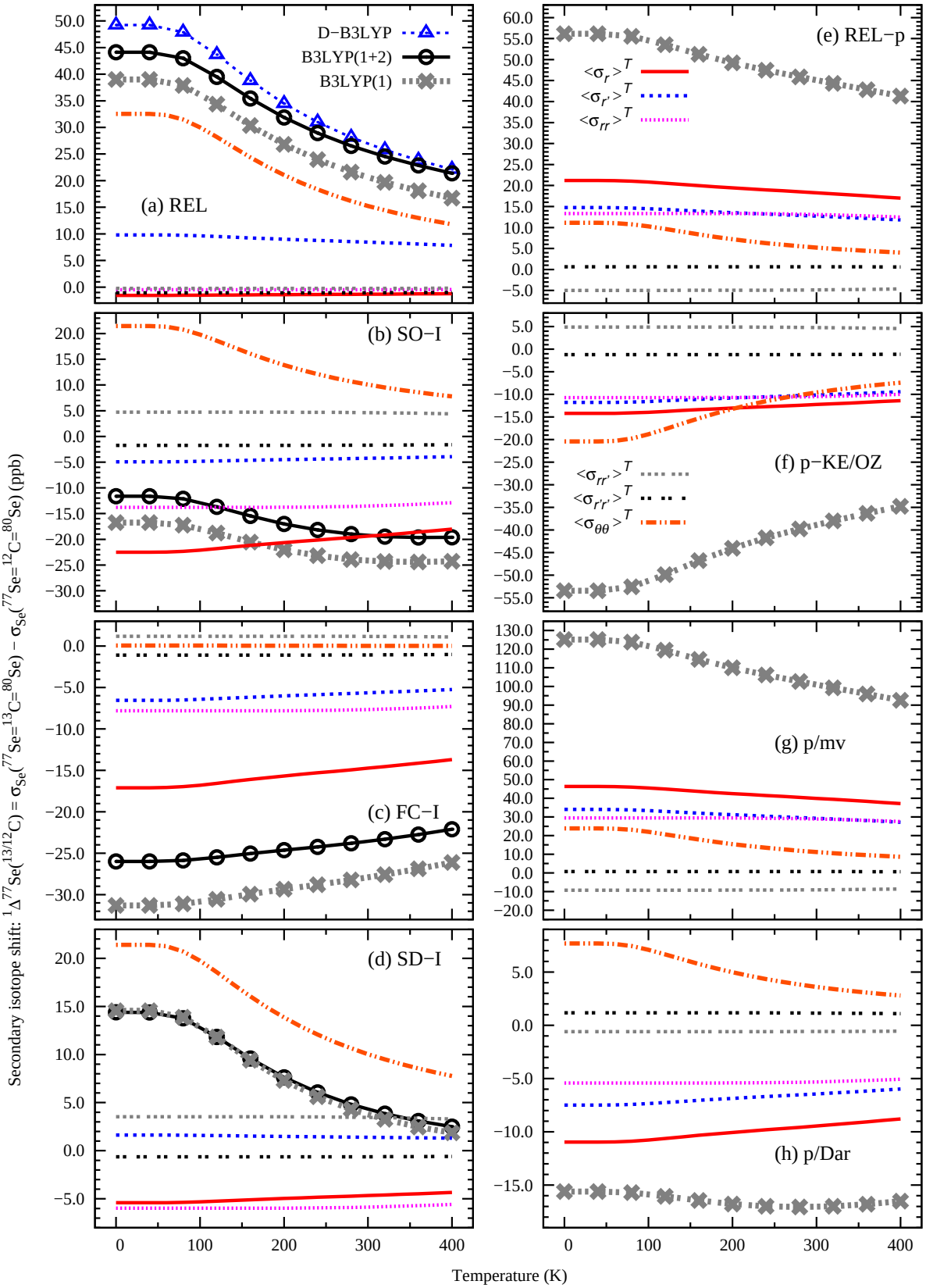

Figure 4. As in Fig. 2, but for the one-bond secondary ^{77}Se isotope shift: $^1\Delta^{77}\mathrm{Se}(^{13/12}\mathrm{C}) = \sigma_{\mathrm{Se}}(^{77}\mathrm{Se}=^{13}\mathrm{C}=^{80}\mathrm{Se}) - \sigma_{\mathrm{Se}}(^{77}\mathrm{Se}=^{12}\mathrm{C}=^{80}\mathrm{Se})$ (the E'-E splitting in Ref. [4]).

Table III. Temperature derivatives of the secondary isotope shifts of CSe_2 at room temperature.[a]

	$d\,{}^2\Delta^{77}\mathrm{Se}_{\mathrm{E-D}}/dT$		$d\,{}^1\Delta^{77}\mathrm{Se}_{\mathrm{E'-E}}/dT$		$d\,{}^1\Delta^{13}\mathrm{C}_{\mathrm{E-D}}/dT$	
NR/REL[b]	NR	TOTAL	NR	TOTAL	NR	TOTAL
KT2/KT2	-0.041	-0.042	-0.737	-0.785	-0.0035	-0.0010
BLYP/BLYP	-0.043	-0.044	-0.774	-0.826	-0.0040	-0.0015
B3LYP/B3LYP	-0.047	-0.048	-0.807	-0.857	-0.0052	-0.0024
B3LYP/B3LYP(1+2)[c]	-0.047	-0.048	-0.807	-0.859	-0.0052	-0.0027
B3LYP/D-B3LYP[d]	-0.047	-0.048	-0.807	-0.868	-0.0052	-0.0030
BHandHLYP/BHandHLYP	-0.053	-0.054	-0.845	-0.893	-0.0071	-0.0038
MP2/B3LYP	-0.021	-0.022	-0.574	-0.624	0.0011	0.0039
CCSD/B3LYP	-0.045	-0.046	-0.725	-0.775	-0.0059	-0.0033
CCSD(T)/B3LYP	-0.038	-0.040	-0.671	-0.721	-0.0039	-0.0009
CCSD(T)/B3LYP(1+2)[c]	-0.038	-0.040	-0.671	-0.723	-0.0039	-0.0014
CCSD(T)/D-B3LYP[d]	-0.038	-0.040	-0.671	-0.732	-0.0039	-0.0018
CCSD(T)/D-B3LYP/FF(VQZ)[e]	-0.043	-0.045	-0.704	-0.766	-0.0044	-0.0015
Exp.[f]		-0.040		-0.80		-0.002

[a] In ppb/K. Experimental results from Ref. [4]. Theoretical results with CCSD(T)/V5Z force field and only 1-electron SO-I terms included in relativistic BPPT correction, if not otherwise noted. Derivatives obtained by fitting in the $T = 270$ K ... 310 K interval.
[b] Nonrelativistic/relativistic method. [c] Both 1- and 2-electron SO-I terms included in the relativistic BPPT contribution. [d] Four-component D-DFT relativistic contribution at the D-DFT/B3LYP level. [e] With CCSD(T)/VQZ force field. [f] Ref. [4]. Experimental result obtained in C_6D_6 solvent.

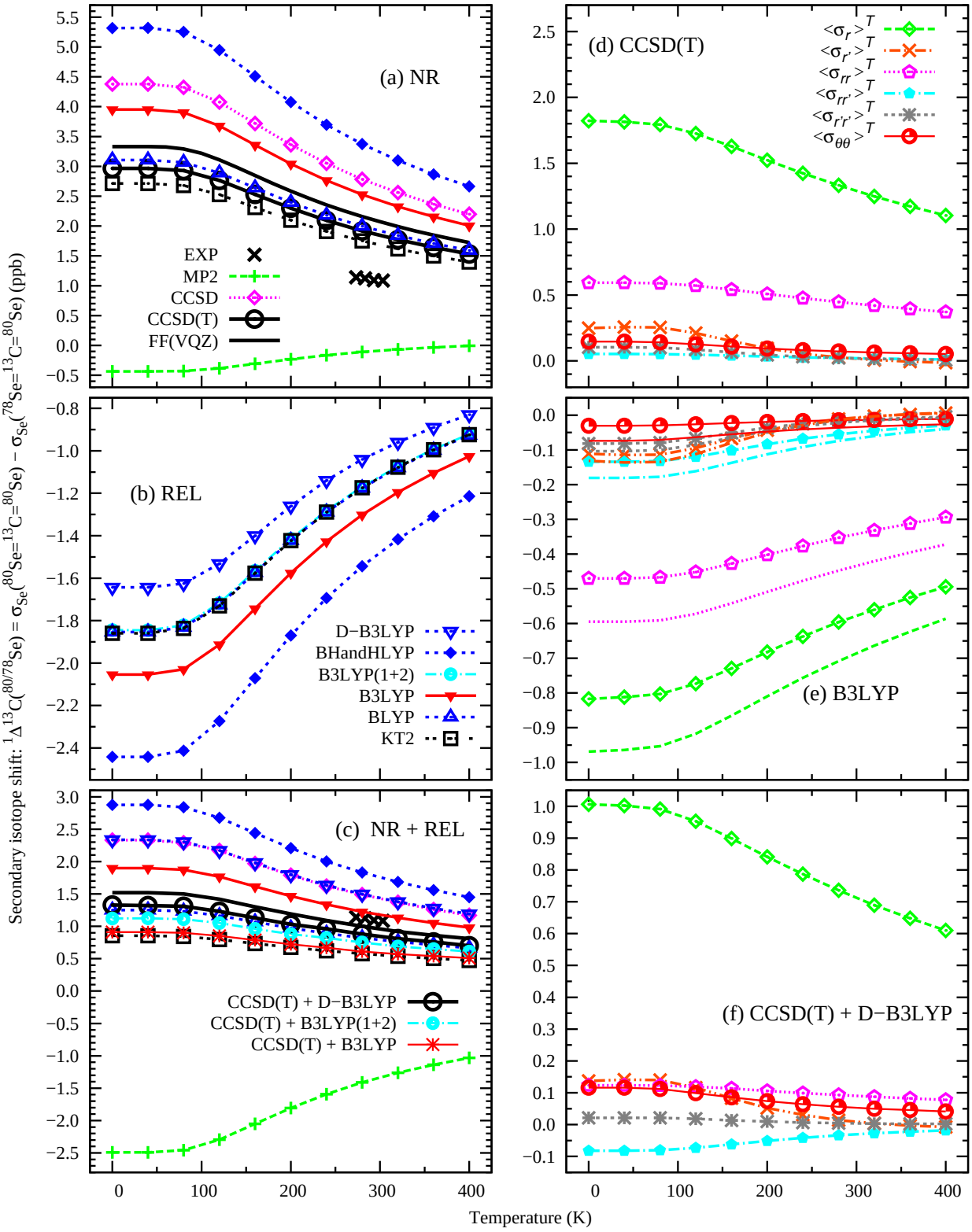

Figure 5. As in Fig. 1, but for the one-bond secondary ^{13}C isotope shift: $^{1}\Delta^{13}C(^{80/78}Se) = \sigma_C(^{80}Se{=}^{13}C{=}^{80}Se) - \sigma_C(^{78}Se{=}^{13}C{=}^{80}Se)$ (the E-D splitting in Ref. [4]).

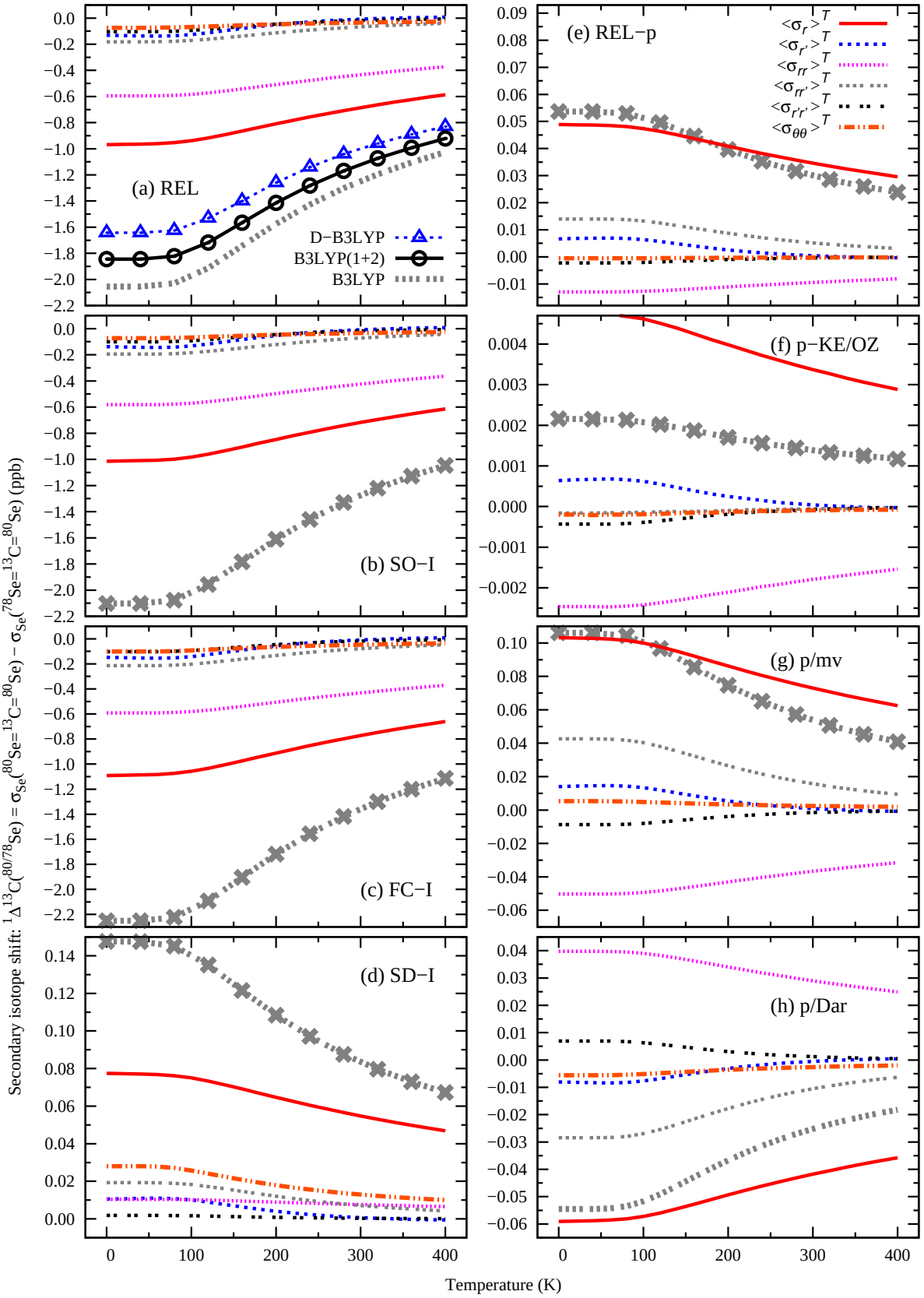

Figure 6. As in Fig. 2, but for the one-bond secondary ^{13}C isotope shift:$^1\Delta^{13}C(^{80/78}Se)=\sigma_C(^{80}Se=^{13}C=^{80}Se)-\sigma_C(^{78}Se=^{13}C=^{80}Se)$ (the E-D splitting in Ref. [4]).

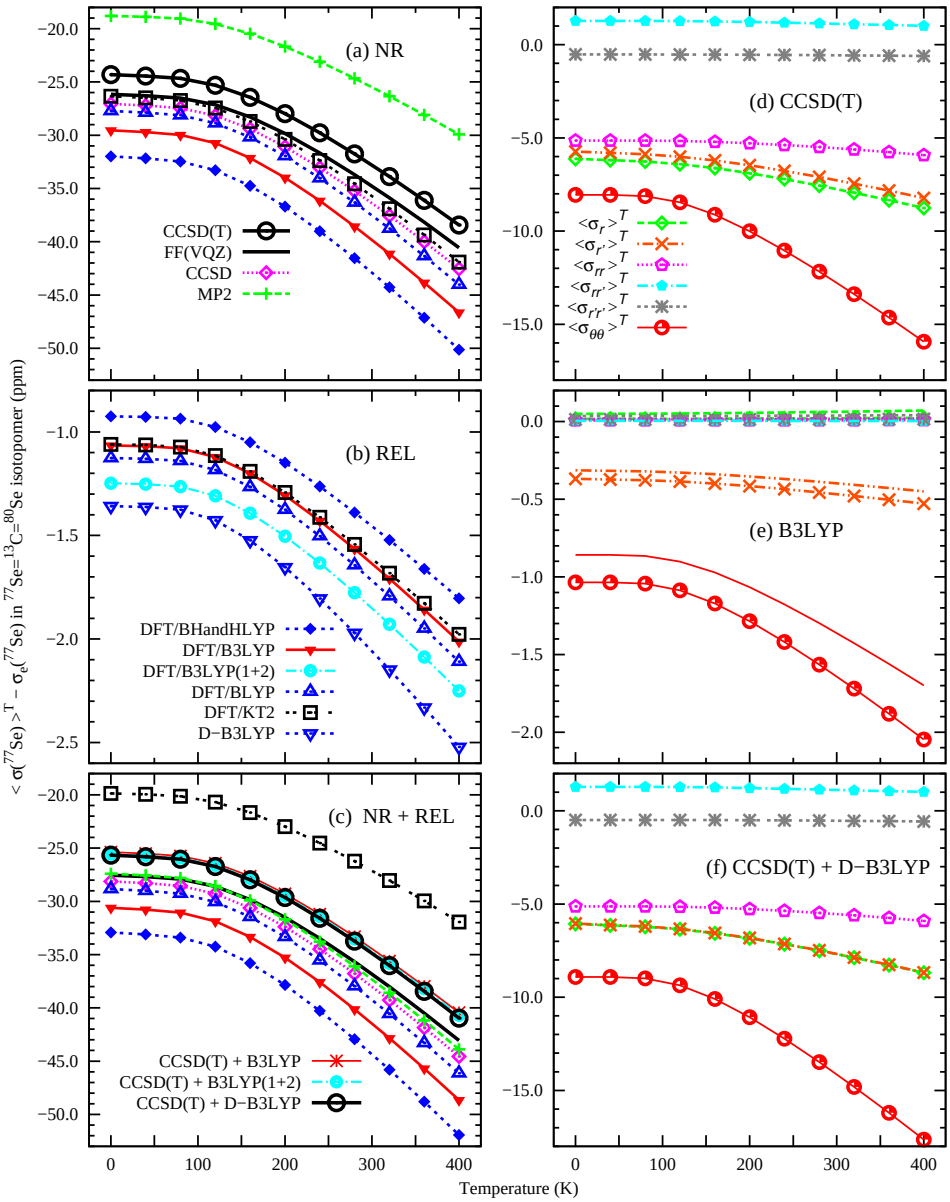

Figure 7. The temperature dependence of ^{77}Se shielding constant in the ^{77}Se = ^{13}C = ^{80}Se isotopomer at different electron correlation treatment levels. (a) The nonrelativistic (NR) level. (b) Relativistic corrections at the 4-component (D-B3LYP) as well as 1- and 2-electron [B3LYP(1+2)] BPPT levels of theory; with different DFT functionals. (c) The total results containing NR-data with CCSD(T), and the relativistic BPPT(1) contributions at the B3LYP level. The NR CCSD(T) result is also shown with BPPT corrections including both 1- and 2-electron spin-orbit contributions [B3LYP(1+2)]. Also NR+BPPT(1) results with different DFT functionals are displayed. Individual rovibrational contributions at CCSD(T)+D-B3LYP level for nonrelativistic/relativistic terms are displayed in panels (d)-(f), referencing to the terms in Eq. (2) in the article. In panel (e), the lines without symbols are B3LYP(1) results. FF(VQZ) denotes CCSD(T)+D-B3LYP results with the CCSD(T)/VQZ force field.

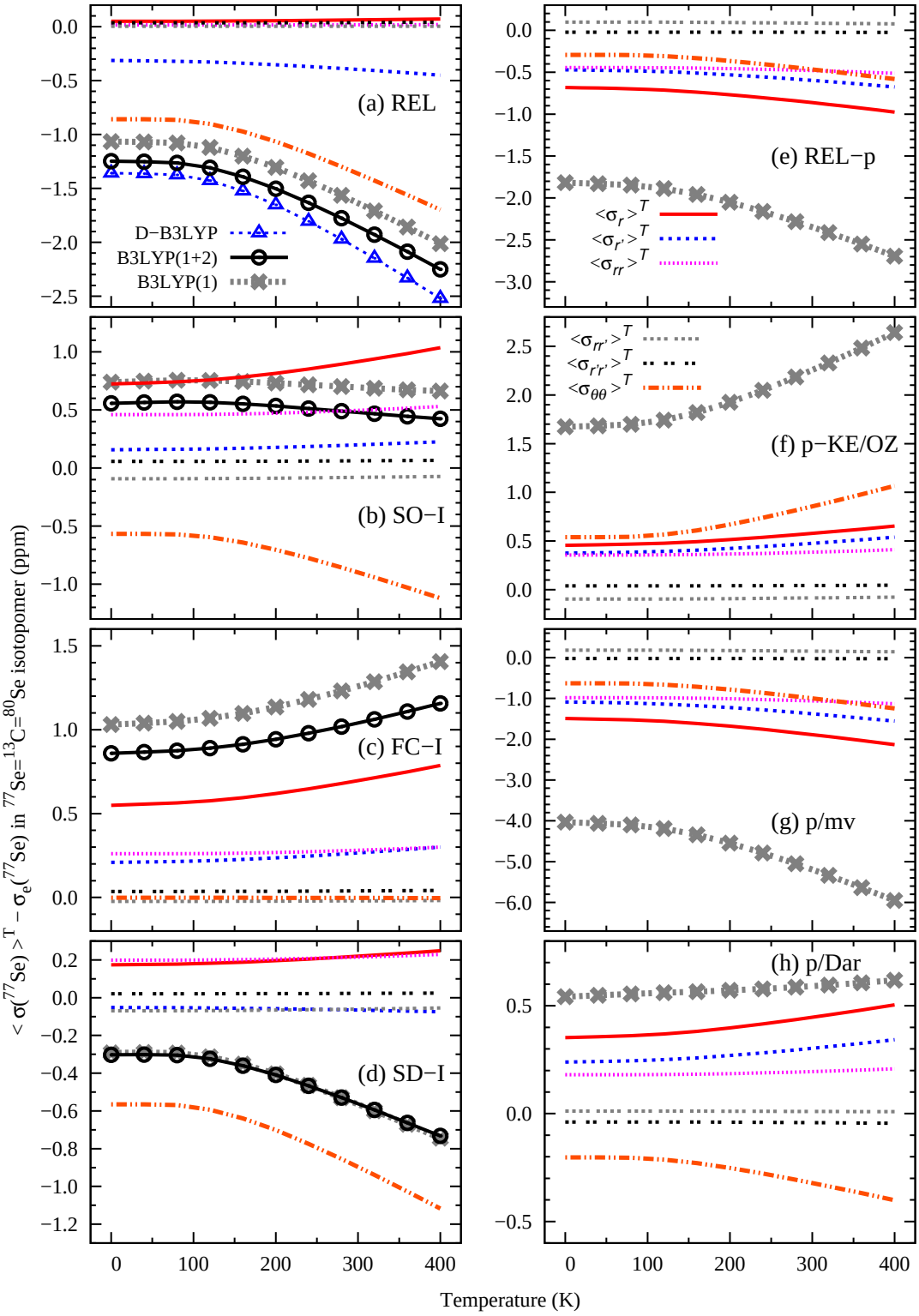

Figure 8. The temperature dependence of the main relativistic BPPT-5 contributions to the ^{77}Se shielding constant in the ^{77}Se = ^{13}C = ^{80}Se isotopomer. (a) The full BPPT effect. (b) Third-order spin-orbit (SO-I) contribution, a sum of (c) FC-I and (d) SD-I terms. (e) The scalar relativistic (REL-p), a sum of the relativistic paramagnetic contributions in panels (f)-(h). Rovibrational contributions at B3LYP level are displayed in each panel.

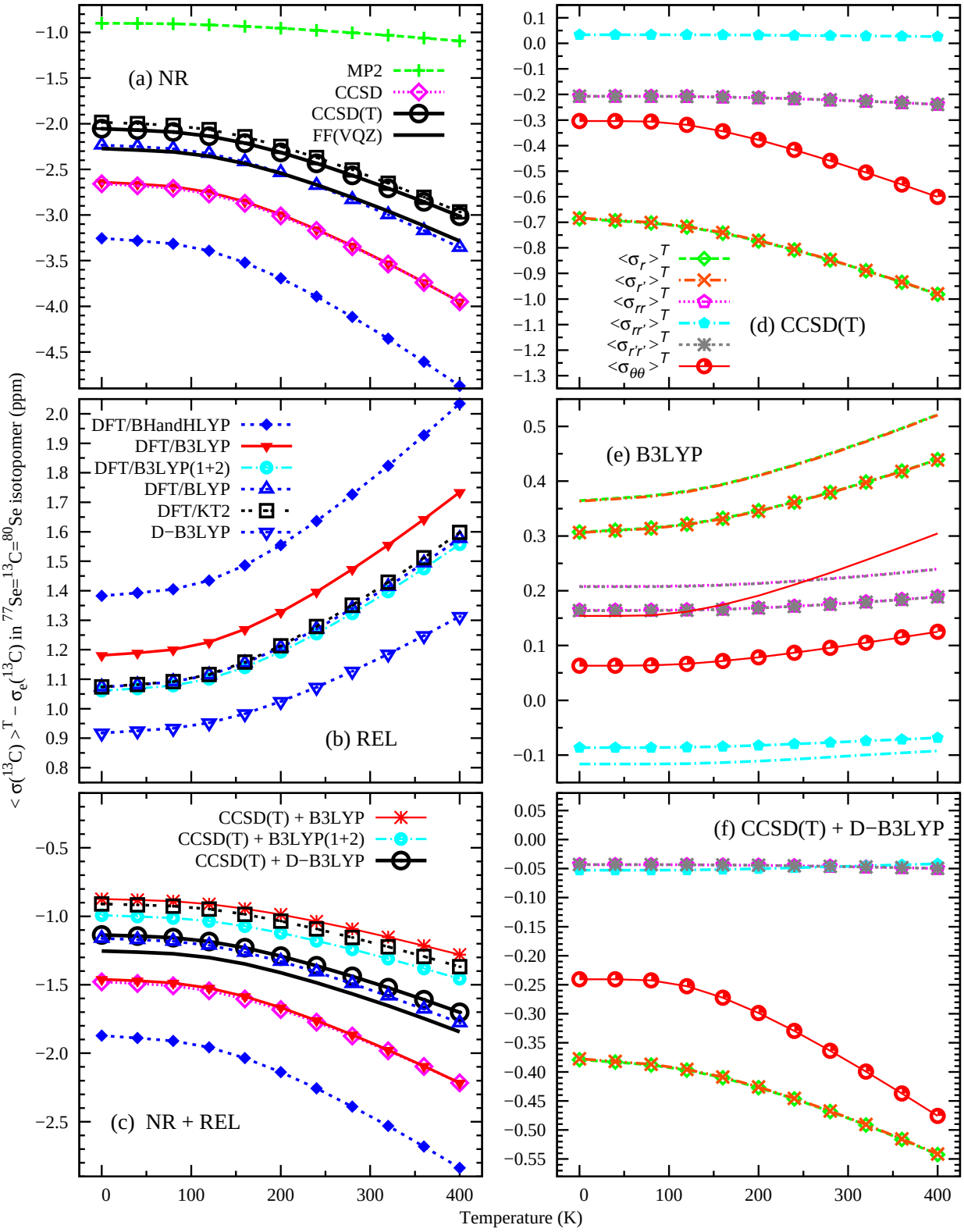

Figure 9. As in Fig. 7, but for the ^{13}C shielding constant in the ^{77}Se = ^{13}C = ^{80}Se isotopomer.

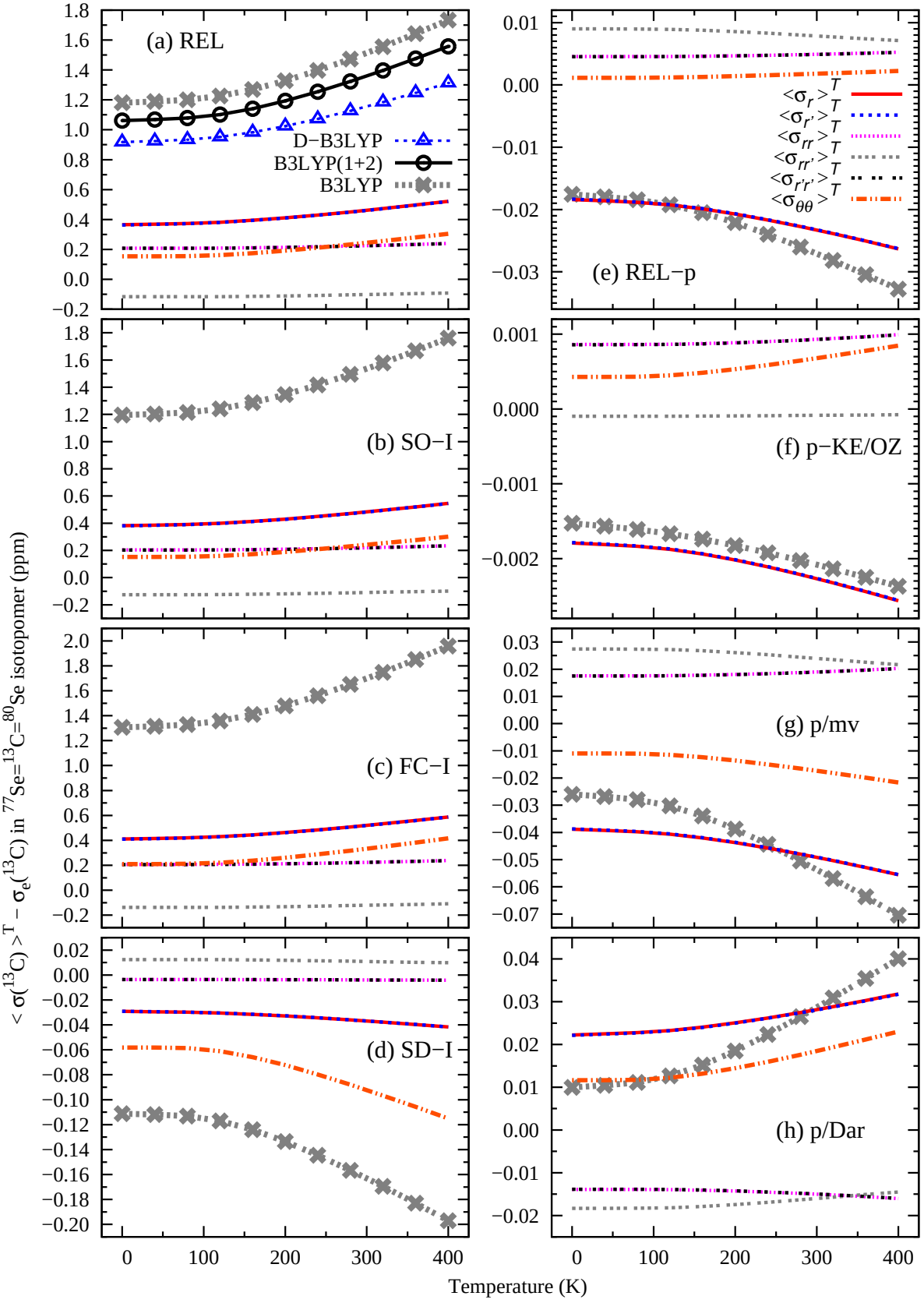

Figure 10. As in Fig. 8, but for the ^{13}C shielding constant in the ^{77}Se = ^{13}C = ^{80}Se isotopomer.

Table IV. Parameters of the property hypersurfaces for the absolute ^{77}Se nuclear shielding constant at equilibrium geometry of the CSe_2 molecule.[a]

Derivative	KT2	BLYP	B3LYP	BHandHLYP	MP2	CCSD	CCSD(T)
σ_r^{NR}	-1670.4	-1748.7	-1874.6	-2049.9	-925.5	-1627.2	-1443.9
$\sigma_{r'}^{\mathrm{NR}}$	-1391.2	-1458.8	-1571.1	-1742.9	-940.6	-1540.3	-1358.5
$\sigma_{rr}^{\mathrm{NR}}$	-8021.0	-8489.3	-9321.6	-10559.5	-4809.3	-8715.8	-7517.3
$\sigma_{r'r'}^{\mathrm{NR}}$	-686.0	-665.1	-999.8	-1529.6	420.1	-1310.6	-771.1
$\sigma_{rr'}^{\mathrm{NR}}$	-1874.1	-1863.6	-2114.7	-2562.7	485.3	-2089.7	-1589.8
$\sigma_{\theta\theta}^{\mathrm{NR}}$	-1405.3	-1474.1	-1507.5	-1526.2	-1178.7	-1333.1	-1266.0
Derivative	KT2[b]	BLYP[b]	B3LYP[b]	BHandHLYP[b]	B3LYP(1+2)[c]	D-B3LYP[d]	
σ_r^{REL}	-1.5	-0.1	11.7	34.1	-13.1	4.0	
$\sigma_{r'}^{\mathrm{REL}}$	-64.4	-65.6	-74.2	-85.1	-82.7	-87.2	
$\sigma_{rr}^{\mathrm{REL}}$	-39.7	-50.5	24.3	202.7	-75.8	11.6	
$\sigma_{r'r'}^{\mathrm{REL}}$	63.3	82.7	52.3	0.6	41.6	20.0	
$\sigma_{rr'}^{\mathrm{REL}}$	-19.7	-15.4	-5.6	24.5	-24.8	-8.1	
$\sigma_{\theta\theta}^{\mathrm{REL}}$	-127.8	-138.8	-134.9	-130.3	-131.8	-162.6	

[a] The units are ppm, Å, and rad ($r_e = 1.6881$ Å). [b] BPPT theory with 1-electron contributions. [c] BPPT theory with including also 2-electron SO-I contributions. [d] 4-component Dirac theory.

Table V. Parameters of the property hypersurfaces for the absolute ^{13}C nuclear shielding constant at equilibrium geometry of the CSe_2 molecule.[a]

Derivative	KT2	BLYP	B3LYP	BHandHLYP	MP2	CCSD	CCSD(T)
σ_r^{NR}	-145.3	-167.7	-207.0	-268.0	-26.2	-222.5	-161.8
$\sigma_{rr}^{\mathrm{NR}}$	-275.5	-298.5	-396.5	-553.3	36.0	-458.8	-303.4
$\sigma_{rr}^{\mathrm{NR}}$	-24.2	-47.3	-137.4	-308.5	634.2	-247.6	-41.0
$\sigma_{\theta\theta}^{\mathrm{NR}}$	-62.5	-70.1	-71.8	-75.4	-33.0	-54.7	-47.7
Derivative	KT2[b]	BLYP[b]	B3LYP[b]	BHandHLYP[b]	B3LYP(1+2)[c]	D-B3LYP[d]	
σ_r^{REL}	79.2	80.3	86.0	96.9	77.1	72.5	
$\sigma_{rr}^{\mathrm{REL}}$	259.9	262.4	304.1	382.5	273.8	240.1	
$\sigma_{rr'}^{\mathrm{REL}}$	137.7	126.2	144.7	186.0	129.5	107.5	
$\sigma_{\theta\theta}^{\mathrm{REL}}$	25.1	21.5	24.2	29.9	21.8	9.9	

[a] The units are ppm, Å, and rad ($r_e = 1.6881$ Å). [b] BPPT theory with 1-electron contributions. [c] BPPT theory with including also 2-electron SO-I contributions. [d] 4-component Dirac theory.

Table VI. Temperature dependence of ^{77}Se and ^{13}C shielding constants in CSe_2 at room temperature.[a]

	$d\sigma_{Se}/dT$		$d\sigma_{C}/dT$	
NR/REL method	NR	TOTAL	NR	TOTAL
KT2/KT2	-58	-61	-3.6	-1.7
BLYP/BLYP	-60	-64	-4.1	-2.2
B3LYP/B3LYP	-63	-67	-4.8	-2.7
D-B3LYP[b]	-63	-68	-4.8	-3.4
BHandHLYP/BHandHLYP	-67	-70	-5.9	-3.5
MP2/B3LYP	-41	-45	-0.7	1.3
CCSD/B3LYP	-57	-61	-4.7	-2.8
CCSD(T)/B3LYP/VQZ	-54	-57	-3.7	-1.5
CCSD(T)/B3LYP	-52	-56	-3.5	-1.5
CCSD(T)/B3LYP(1+2)	-52	-56	-3.5	-1.7
CCSD(T)/D-B3LYP	-52	-57	-3.5	-2.0
DFT/PW91[c]	-55		-3.8	
CAS[c]	-60		-3.1	
Exp.[d]				-6.0

[a] In ppm/K. ^{77}Se=^{13}C=^{80}Se isotopomer. Linear fit to results in the $T = 270 \ldots 310$ K range. [b] Relativistic 4-component Dirac calculation with GIAOs. [c] Ref. [4]. [d] Experimental result from Ref. [4] obtained in C_6D_6 solvent.

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