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SI: The Double-Bond Elucidation for the Arsagermene with a Tricoordinate Germanium Center: A Theoretical Survey

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1 GEOMETRIC DETAILS

All systems presented in our work are local minimum configurations in the potential energy surface, not showing any imaginary frequencies. The thermodynamic (ΔG, ΔH, and ZPE) parameters are shown at the bottom of xyz matrix.

$(SiH_3)_2GeAsPh$
Ge -1.808616575 1.109562530 -0.067368724
Si -2.770006395 0.804967576 2.099094595
Si -3.176273565 1.081261350 -2.019125206
H -4.037898444 0.027101904 1.946118974
H -3.101883021 2.116219649 2.730221518
H -1.818394154 0.051428709 2.961896455
H -2.312311295 1.245846722 -3.224114135
H -4.174719049 2.192102177 -1.971453985
H -3.918671397 -0.211892069 -2.111478462
As 0.434543688 1.390953474 -0.275857122
C 0.730435328 1.385576145 1.677541279
C 1.437122012 0.327084918 2.268700509
C 0.238719806 2.416333444 2.495483431
C 0.425927254 2.373179008 3.879584981
C 1.109903630 1.303977773 4.462327575
C 1.618661407 0.283991794 3.652963178
H 1.828698622 -0.479200679 1.646694577
H 2.155674320 -0.552612757 4.101521325
H 0.031018656 3.176025727 4.503107149
H 1.249955444 1.266611193 5.542695176
H -0.296254275 3.253942411 2.046524911
ΔG = -5127.79097650 Eh
ΔH =-5127.73464403 Eh
ZPE = 0.13719580 Eh

$(OCH_3)_2GeAsOCH_3$
Ge -2.040779644 0.749990514 -0.213929469
O -2.952020864 1.466292658 1.145376389
O -3.164787646 0.864424868 -1.614533603
C -4.313911438 1.898691231 0.974778282
C -2.682526762 0.427433702 -2.894167271
H -4.624029804 2.331789888 1.934218559
H -4.976500164 1.056658001 0.728297635
H -4.402396494 2.658830774 0.185715108
H -3.505764964 0.547733618 -3.609899666
H -2.382932177 -0.632777076 -2.877156019
H -1.826955643 1.034658865 -3.231751371
As 0.227205717 0.188866491 -0.332285263
O 0.677689206 0.453047274 1.414322233
C 0.591124943 1.780614132 1.942786917
H 1.138455224 1.781383647 2.895891579
H -0.460270255 2.058195774 2.131661731
H 1.037814766 2.524038639 1.263596228
ΔG = -4658.94310031 Eh
ΔH = -4658.88785028 Eh
ZPE = 0.12202786 Eh

$(CH_3)_2GeAsCH_3$
Ge -2.080640000 0.906992000 -0.161580000
C -2.997629000 0.825361000 1.585523000
C -3.367228000 0.704601000 -1.640527000
H -3.744605000 1.627820000 1.641874000
H -2.285942000 0.937300000 2.410113000
H -3.512391000 -0.139478000 1.681350000
H -2.842312000 0.751302000 -2.600791000
H -4.116223000 1.506096000 -1.597849000
H -3.885049000 -0.259839000 -1.557338000
As 0.117868000 1.187524000 -0.573339000
C 0.779629000 1.316231000 1.324233000
H 1.510432000 0.515263000 1.486986000
H -0.019278000 1.228907000 2.067097000
H 1.280137000 2.283946000 1.447246000
ΔG = -4433.16932230 Eh
ΔH = -4433.12228089 Eh
ZPE = 0.10709421 Eh

H_2GeAsH

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Ge -2.16955836887685 0.92034661120312 -0.05910287638695
H -2.97547621706058 1.03025729186930 1.25450142191314
H -3.10626124820812 0.81602663593019 -1.28288956335809
As 0.06806287564966 0.90454990428276 -0.27543796324509
H 0.19482595849590 1.03366655671464 1.25355298107699
ΔG = -4315.22512471 Eh
ΔH = -4315.19340419 Eh
ZPE = 0.02147752 Eh

$(OH)_2GeAsOH$
Ge -2.095383425 0.915649877 -0.160414892
O -3.064728645 1.478737250 1.229278791
O -3.306451043 1.003338966 -1.493244410
H -3.977541697 1.644133815 0.931242180
H -2.951752251 0.684485736 -2.339875367
As 0.158102036 0.311044939 -0.194720684
O 0.472700686 0.449291542 1.610933606
H 0.706406340 1.372139875 1.806087776
ΔG = -4541.07929397 Eh
ΔH = -4541.03585640 Eh
ZPE = 0.04028669 Eh

$(NH_2)_2GeAsNH_2$
Ge -2.109713176 0.974533432 -0.273595400
N -2.996714316 1.486156311 1.249081525
N -3.416593398 0.857313195 -1.565593861
H -3.890120983 1.023794818 1.411629324
H -2.381964031 1.377702778 2.058032045
H -3.083489991 0.782783965 -2.524186901
H -4.145639891 1.567019405 -1.505640012
As 0.168006039 0.636719728 -0.279138274
N 0.138211917 0.861397724 1.643879869
H 0.739808005 1.649718606 1.887782256
H 0.536990824 0.026922039 2.077082427
ΔG = -4481.38794546 Eh
ΔH = -4481.34447105 Eh
ZPE = 0.07649437 Eh

F_2GeAsF
Ge -2.16679799995884 0.91922152096848 -0.08567346514250
F -3.20219480146125 1.03722547430712 1.31118540147531
F -3.28816129680084 0.80621243611686 -1.42067389198349
As 0.14071599531221 0.89710740194116 -0.32399075759597
F 0.52803210290872 1.04508116666637 1.40977571324665
ΔG = -4613.20402609 Eh
ΔH = -4613.16294519 Eh
ZPE = 0.00667234 Eh

$Cl_2GeAsCl$
Ge -2.11460913536193 0.91440634267960 -0.16800679090870
Cl -3.23736583774612 1.05985236663778 1.65780531452945
Cl -3.48954922671050 0.77665944813549 -1.82463226293839
As 0.16396792776369 0.88989912042355 -0.45569947964057
Cl 0.68914927205486 1.06402972212358 1.68115721895820
ΔG = -5694.36763237 Eh
ΔH = -5694.32299242 Eh
ZPE = 0.00447835 Eh

$Br_2GeAsBr$
Ge -2.10228311964563 0.91308372107267 -0.18548459111980
Br -3.27601166684166 1.06781780171255 1.78991814695283
Br -3.55897569709250 0.76190950849240 -1.97652255233194
As 0.16917838567713 0.88966570461974 -0.50726845831829
Br 0.77968509790266 1.07237126410264 1.76998045481720
ΔG = -12036.90268540 Eh
ΔH = -12036.85417706 Eh
ZPE = 0.00341743 Eh

$(OH)_2GeAsCN$
Ge -1.162759000 0.250645000 -0.915206000
As 0.962817000 -0.615261000 -0.984452000
O -2.367663000 0.050838000 0.391546000
O -2.030943000 1.250477000 -2.088006000
C 1.226801000 0.193663000 -2.686782000
N 1.510994000 0.637968000 -3.731287000
H -2.041668000 -0.491994000 1.129274000
H -2.925742000 1.444970000 -1.752970000
ΔG = -4558.10052268 Eh
ΔH = -4558.05602359 Eh
ZPE = 0.03521990 Eh

$(OH)_2GeAsBr$
Ge -1.879545000 0.730302000 -0.657939000
O -2.742514000 0.699600000 0.903822000
H -2.093257000 0.570416000 1.621908000
O -3.173239000 0.967583000 -1.856106000
H -4.034786000 1.025502000 -1.404874000
As 0.376297000 0.511086000 -1.029107000
Br 0.766190000 0.282179000 1.343525000
ΔG = -7039.69572504 Eh
ΔH = -7039.65156817 Eh
ZPE = 0.02839663 Eh

$(CH_3)_2GeAsBr$
Ge -1.951428000 0.885610000 -0.529998000
C -2.774221000 0.835202000 1.250458000
H -3.563113000 0.072459000 1.267773000
H -2.007544000 0.595301000 1.994159000
H -3.220149000 1.812461000 1.475282000
C -3.220286000 1.312173000 -1.976493000
H -2.706648000 1.326132000 -2.943592000
H -4.017523000 0.558068000 -1.999209000
H -3.671905000 2.295129000 -1.790491000
As 0.236139000 0.508780000 -1.014338000
Br 0.995266000 0.083997000 1.219807000
ΔG = -6967.74696084 Eh
ΔH = -6967.69959932 Eh
ZPE = 0.07246053 Eh

$(CH_3)_2GeAsCN$
Ge -1.727079000 0.834497000 -1.299715000
C -1.503902000 0.868802000 0.645082000

H -2.183329000 0.136544000 1.100268000
H -0.466472000 0.625655000 0.896071000
H -1.758701000 1.867865000 1.021783000
C -3.547611000 1.251572000 -1.910364000
H -3.602241000 1.214438000 -3.003295000
H -4.252206000 0.525826000 -1.483802000
H -3.829391000 2.254332000 -1.563677000
As -0.090505000 0.366084000 -2.812162000
C 1.168069000 0.113917000 -1.399251000
N 1.974857000 -0.051110000 -0.567346000
ΔG = -4486.15642016 Eh
ΔH = -4486.10940171 Eh
ZPE = 0.07958371 Eh

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2 IMAGES

Below, we provide a complete set of figures describing geometries found with different methodologies, contour maps of the electron density, contour maps of the Laplacian of electron density, contour maps of the electron localization function of the electron density, and contour of deformation densities by means of eigenvalues for the R_2Ge=AsR compounds.

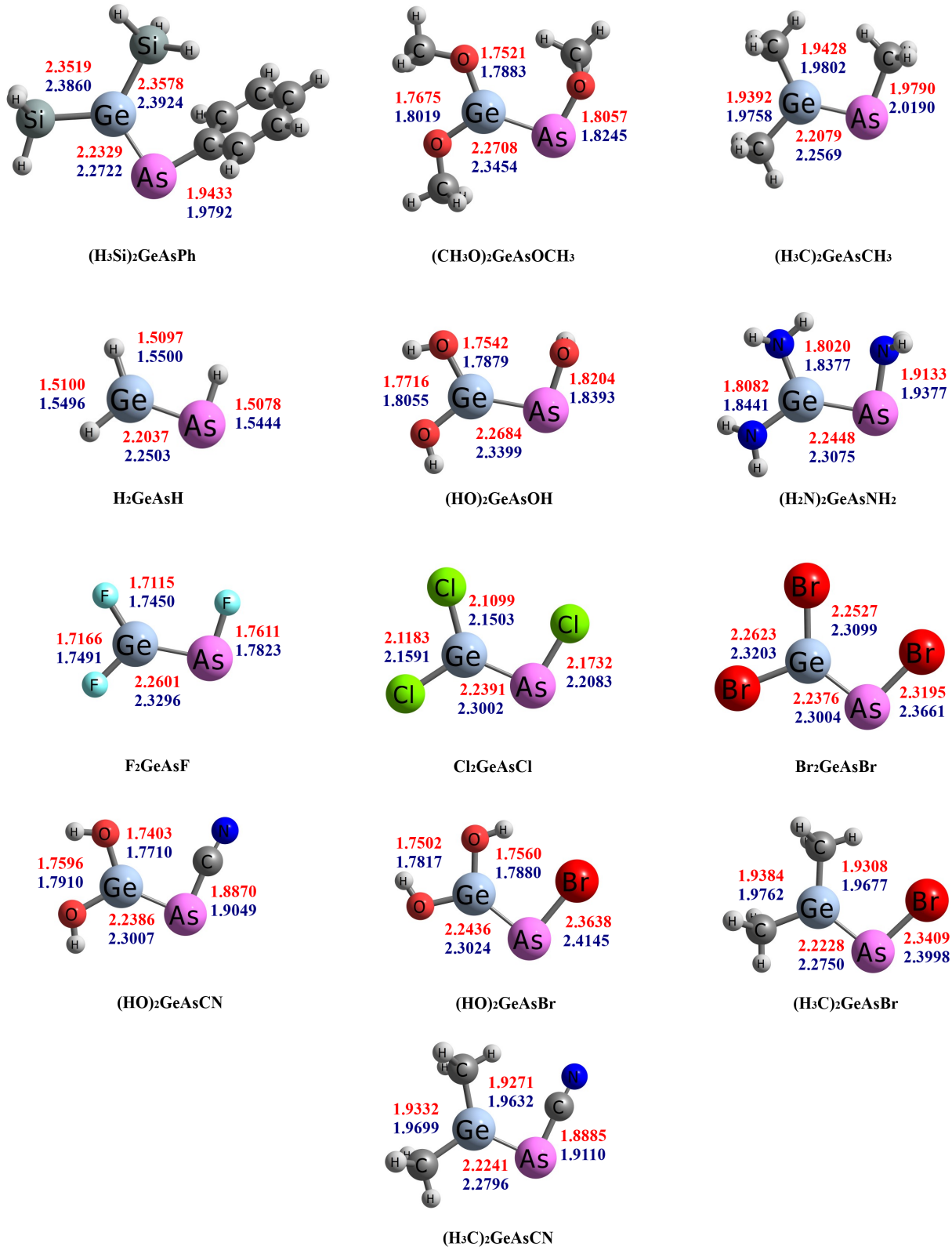

Fig. 1 Molecular structures of $R_2Ge{=}AsR$ compounds. All the values represent the bond lengths (Å), red values from ZORA-RI-MP2/Def2-TZVPP (full-electron) methods, and blue values from RI-BP86-D3BJ/Def2-TZVPP methods. All RI methods employee the same Def2-TZVPP basis set to treat the Coulomb part.

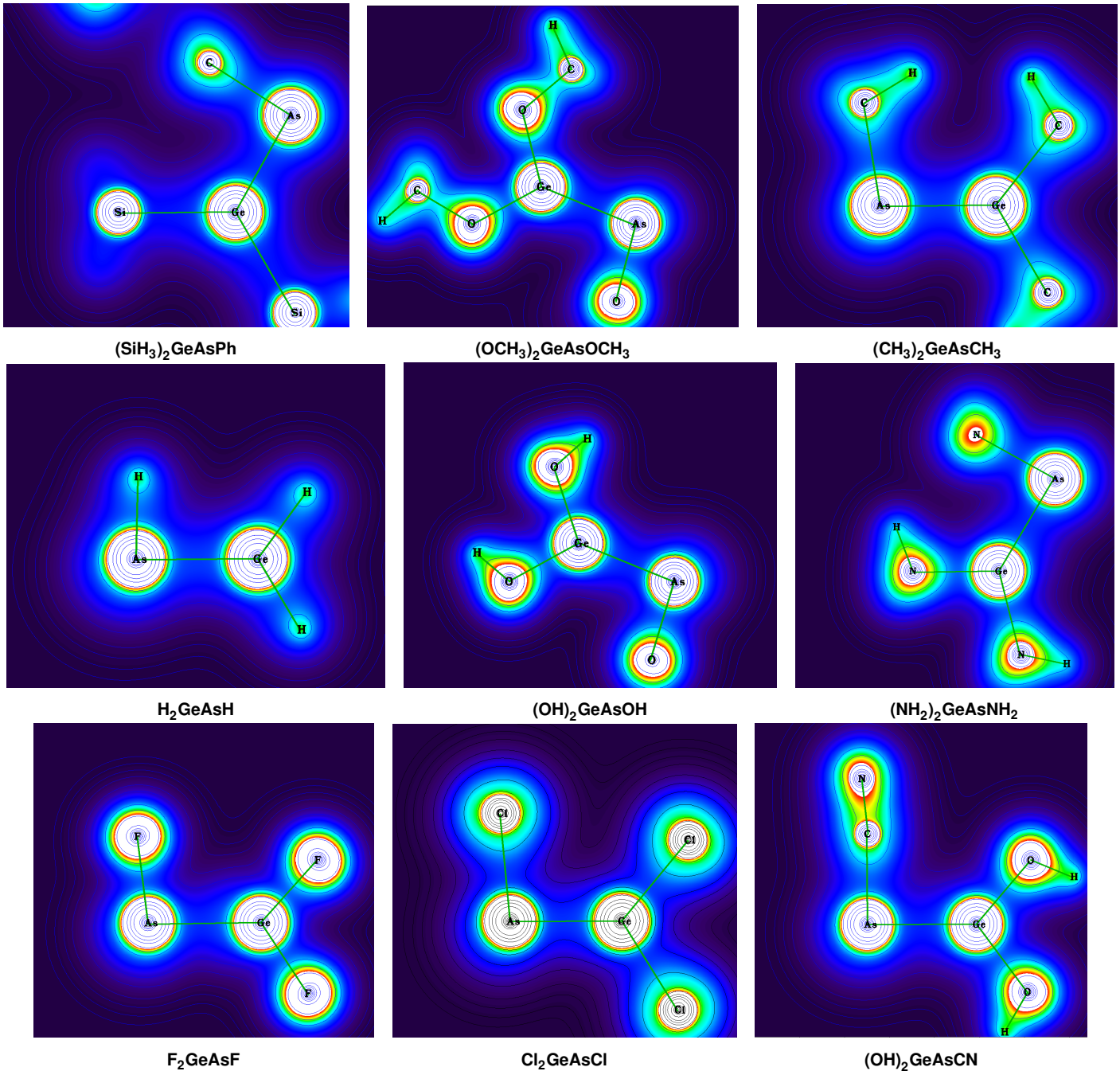

Fig. 2 Contour maps of the electron density ($\rho(r)$) for $R_2Ge{=}AsR$ compounds. Green lines indicate the bond between atoms.

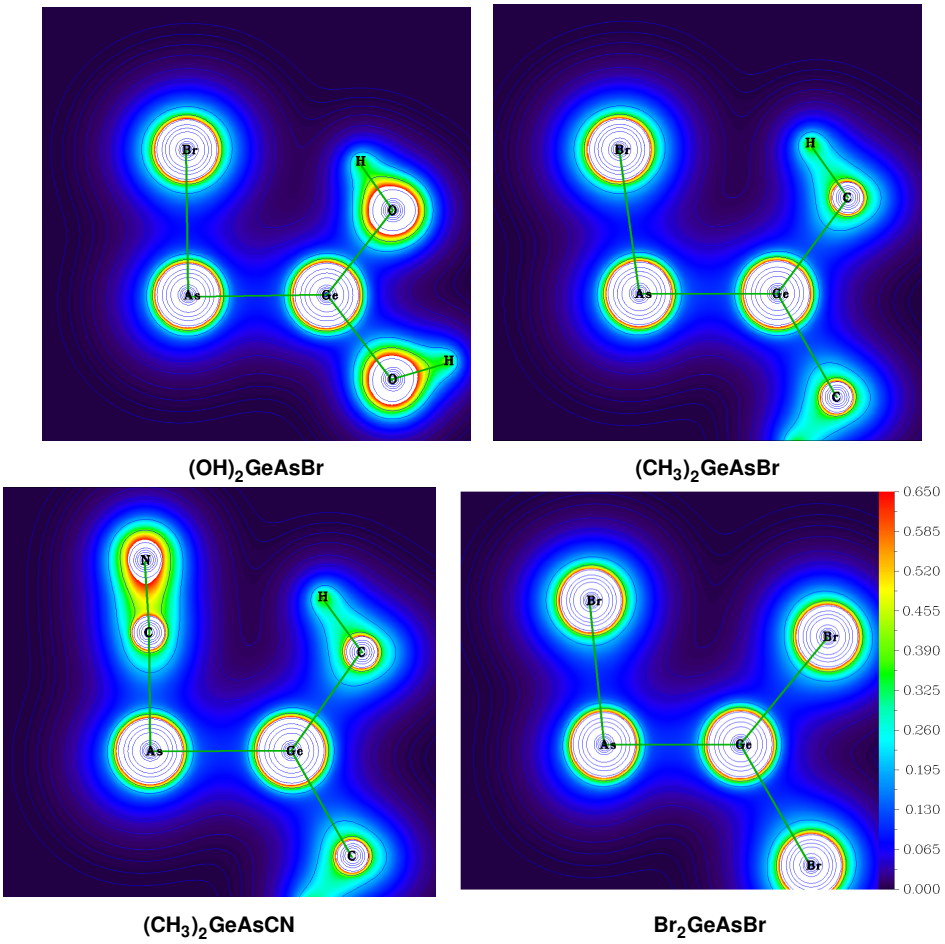

Fig. 3 Contour maps of the electron density ($\rho(r)$) for $R_2Ge{=}AsR$ compounds. Green lines indicate the bond between atoms.

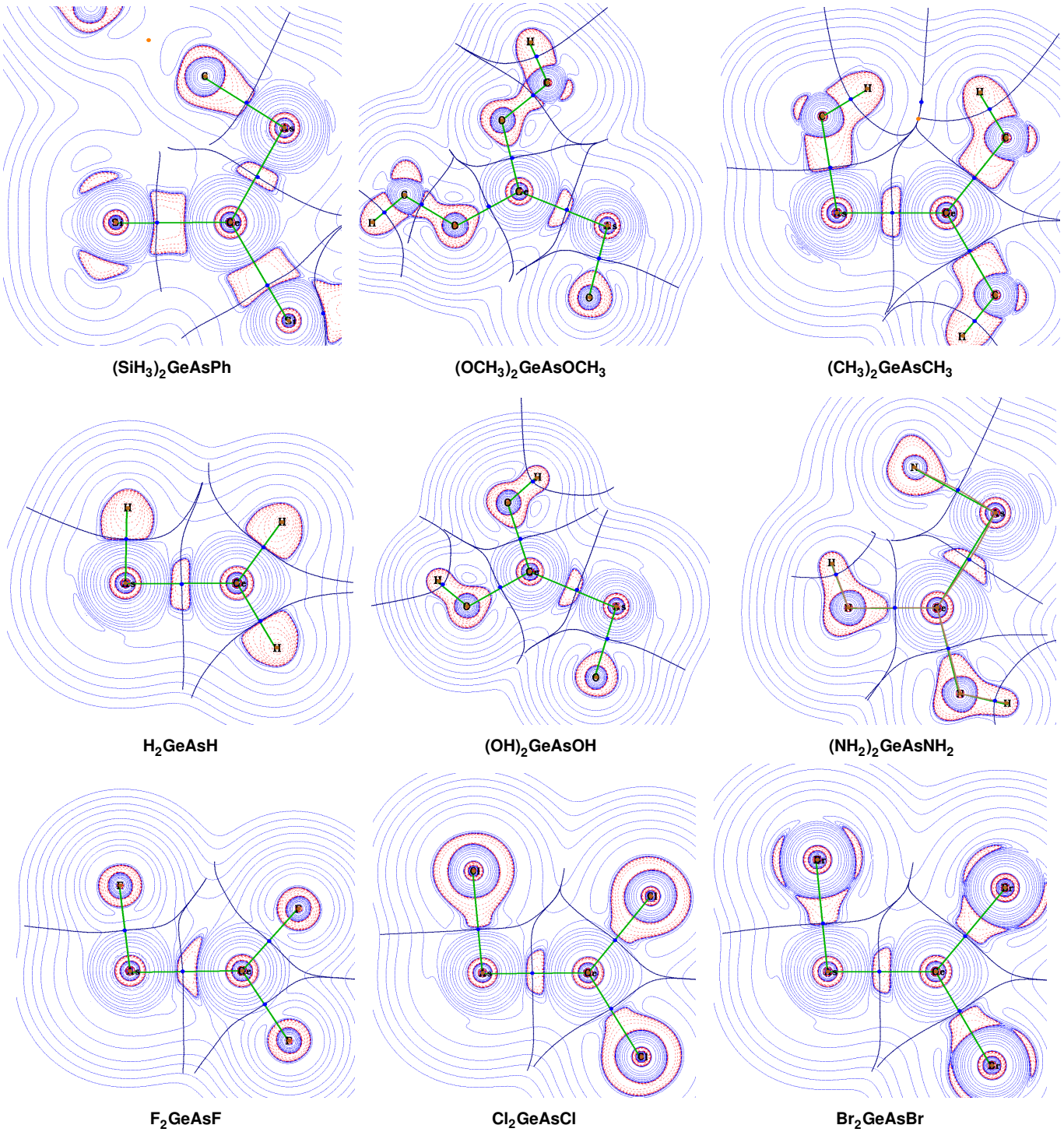

Fig. 4 Contour maps of the Laplacian of electron density ($\nabla^2\rho(r)$) for $R_2Ge{=}AsR$ compounds. The blue lines refer to $\nabla^2\rho(r) > 0$, and the red lines indicate $\nabla^2\rho(r) < 0$. Green lines indicate the bond between atoms, blue dots between them are the bond critical point (BCP), bold blue lines indicate the border of interbasin regions.

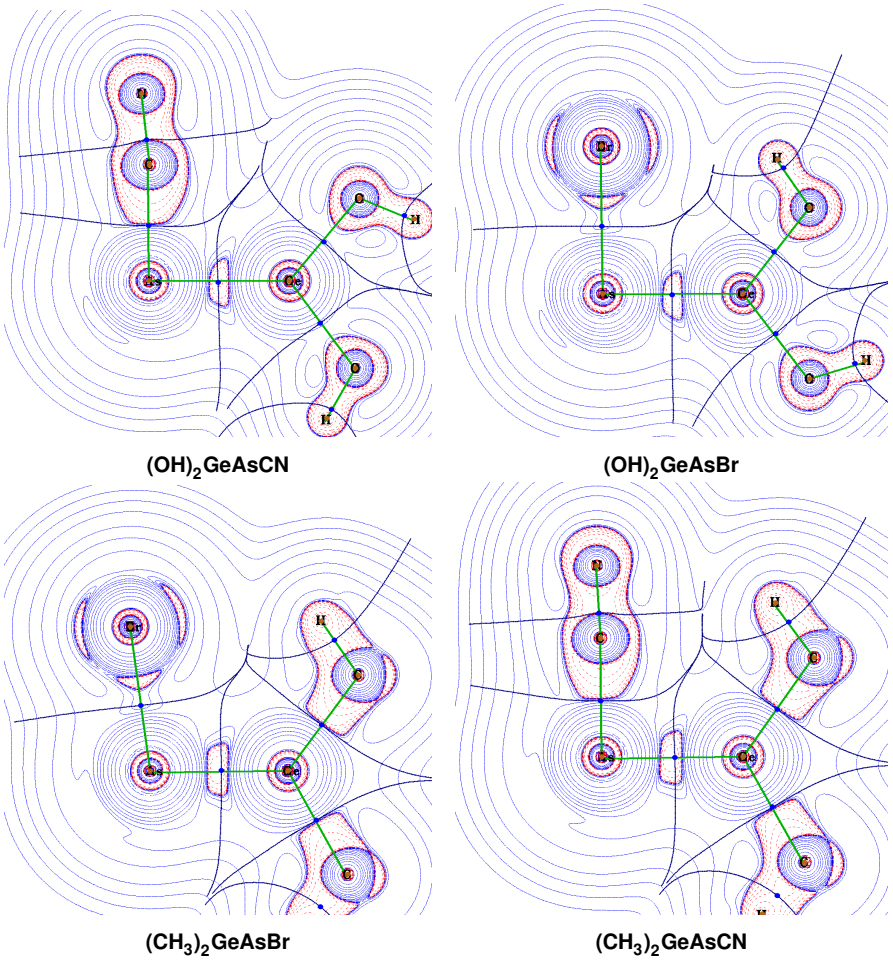

Fig. 5 Contour maps of the Laplacian of electron density ($\nabla^2\rho(r)$) for $R_2Ge{=}AsR$ compounds. The blue lines refer to $\nabla^2\rho(r) > 0$, and the red lines indicate $\nabla^2\rho(r) < 0$. Green lines indicate the bond between atoms, blue dots between them are the bond critical point (BCP), bold blue lines indicate the border of interbasin regions.

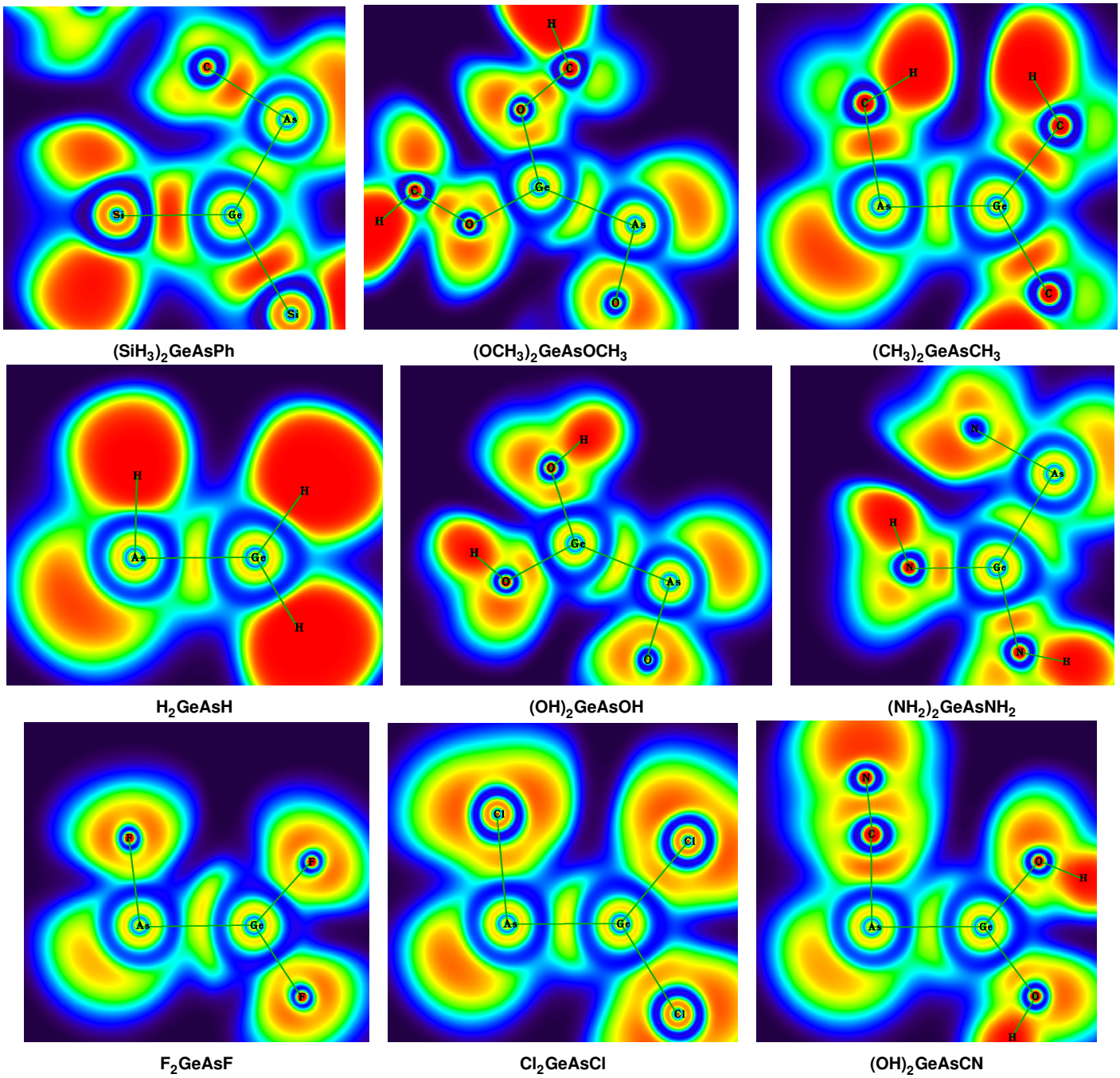

Fig. 6 Contour maps of the electron localization function (ELF) of the electron density for $R_2Ge{=}AsR$ compounds.

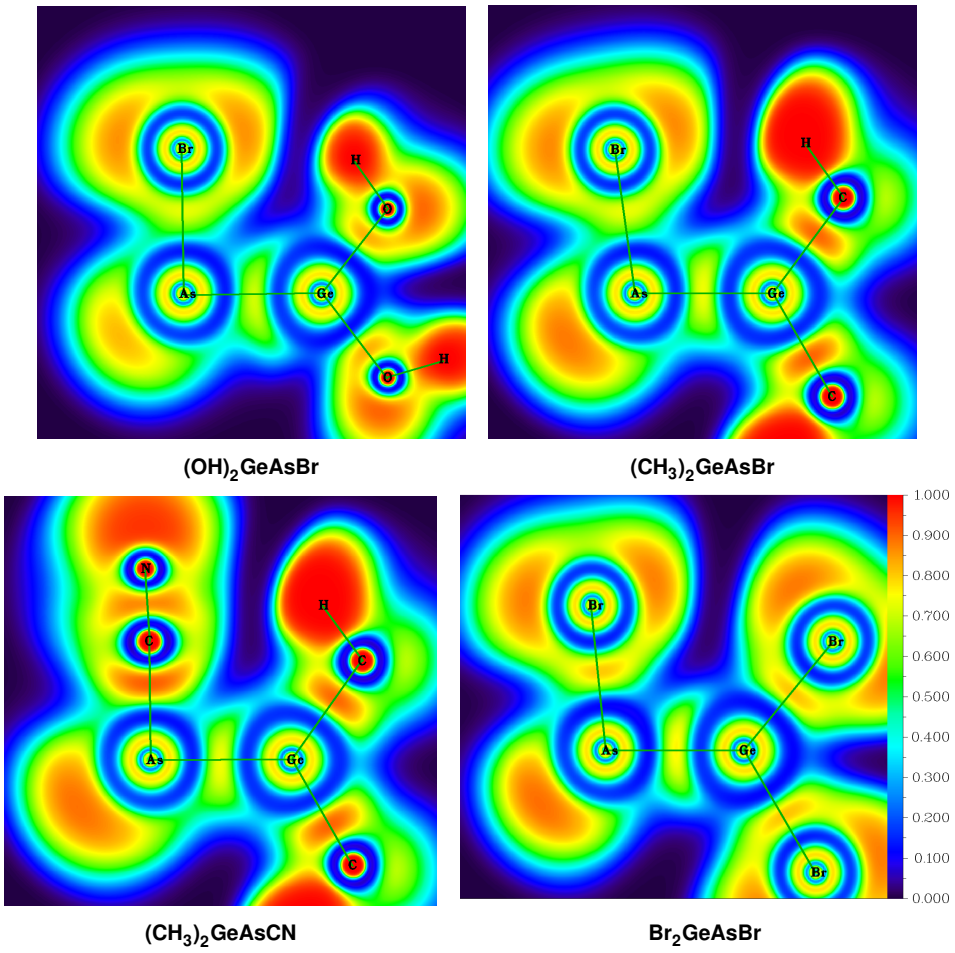

Fig. 7 Contour maps of the electron localization function (ELF) of the electron density for $R_2Ge{=}AsR$ compounds.

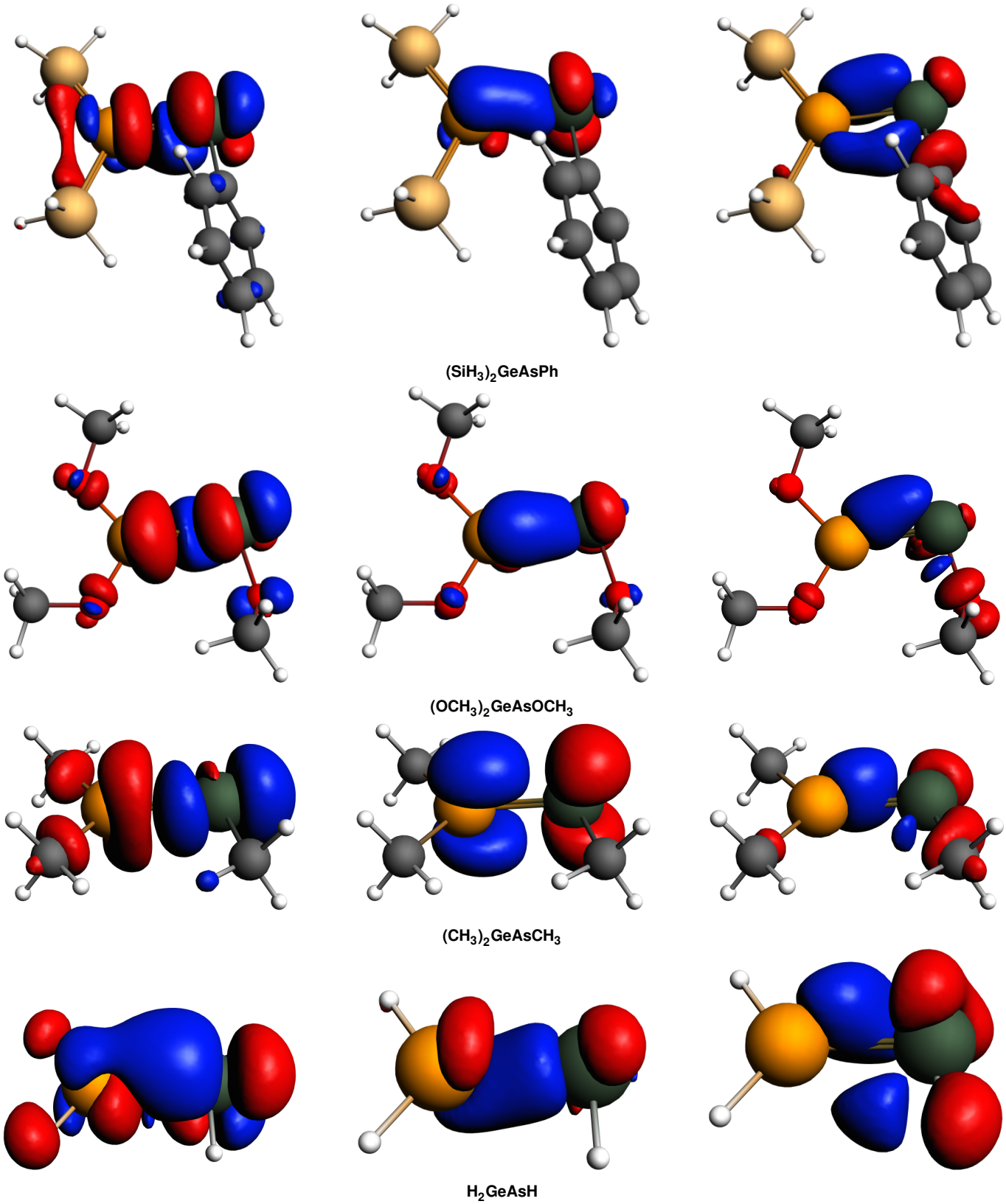

Fig. 8 Contours of deformation densities describing the $R_2Ge{=}AsR$ interactions by means of $\Delta\rho(r)$ eigenvalues. Left, center, and right images denote the $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$ eigenchannels for each compound, respectively. Red surfaces indicate density outflow and blue surfaces density inflow (contour value 0.003 a.u.).

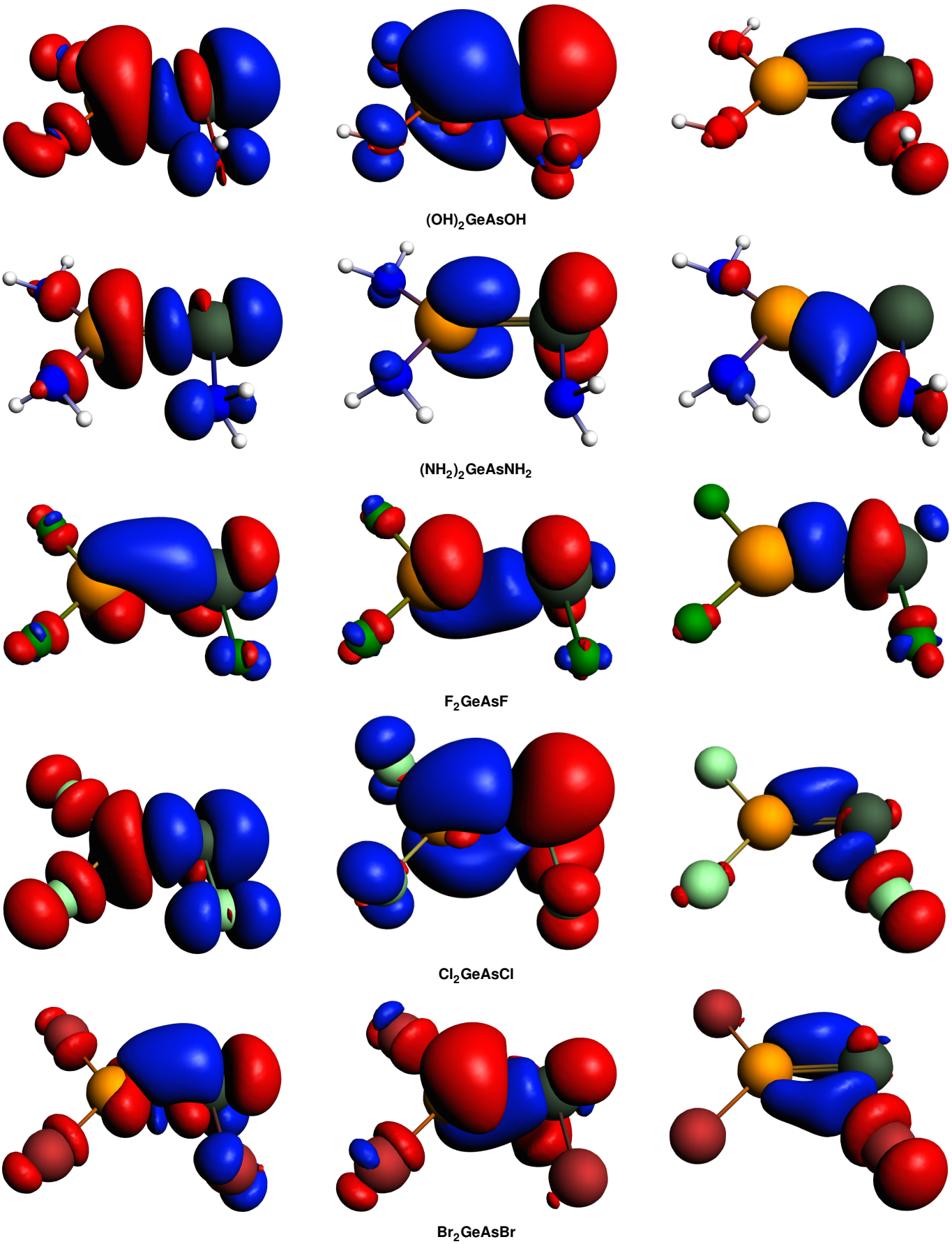

Fig. 9 Contours of deformation densities describing the $R_2Ge{=}AsR$ interactions by means of $\Delta\rho(r)$ eigenvalues. Left, center, and right images denote the $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$ eigenchannels for each compound, respectively. Red surfaces indicate density outflow and blue surfaces density inflow (contour value 0.003 a.u.).

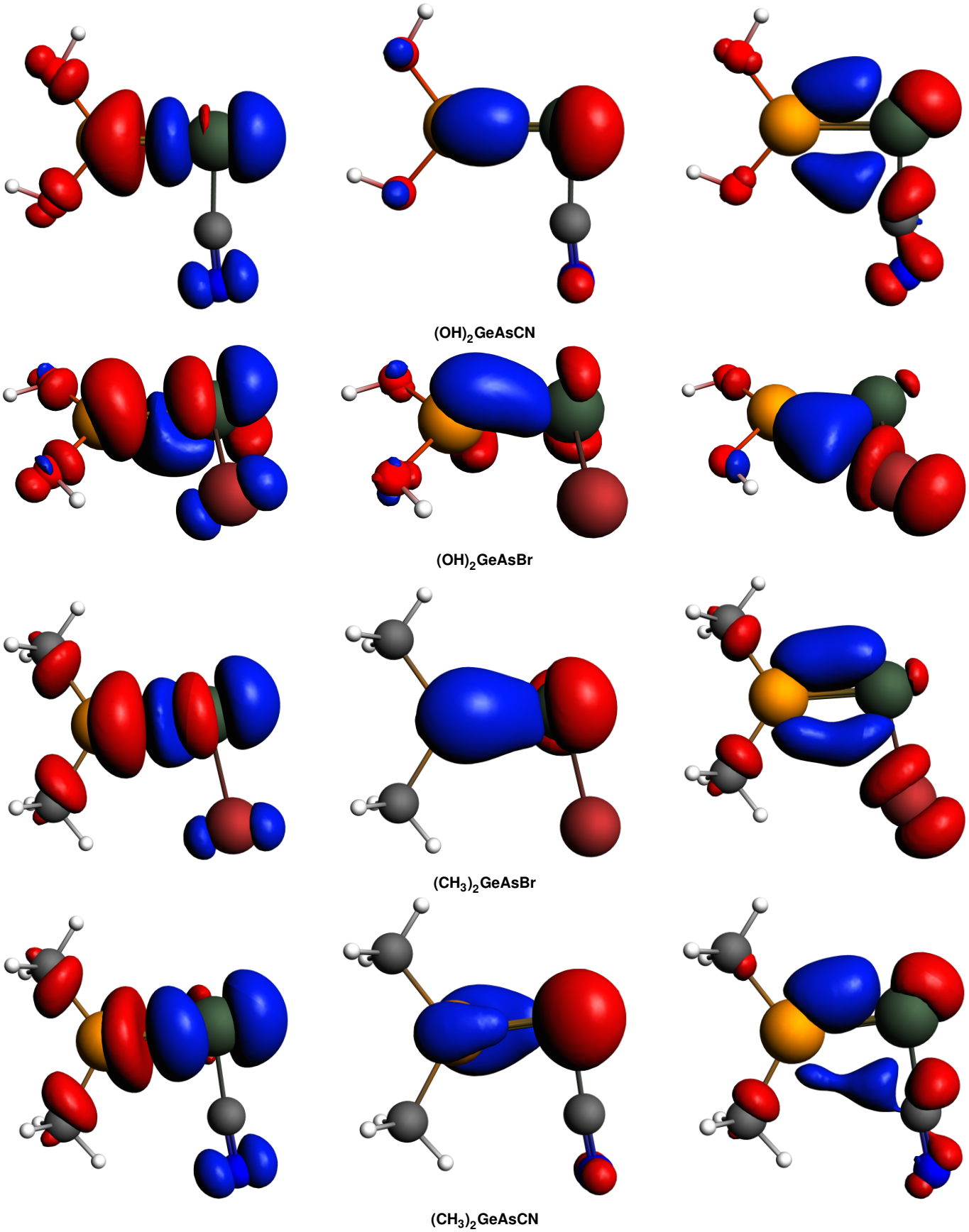

Fig. 10 Contours of deformation densities describing the $R_2Ge{=}AsR$ interactions by means of $\Delta\rho(r)$ eigenvalues. Left, center, and right images denote the $\Delta\rho_1$, $\Delta\rho_2$, and $\Delta\rho_3$ eigenchannels for each compound, respectively. Red surfaces indicate density outflow and blue surfaces density inflow (contour value 0.003 a.u.).

3 TABLE

Below, we provide a table with the energetic EDA-NOCV analysis for the C and D cases.

Table 1 EDA-NOCV of interaction at $R_2Ge{=}AsR$ bond, using BP86-D3BJ/TZ2P as level of theory. The First part (anionic specie as Ge fragment, cationic specie as As fragment **C**), and second part (anionic species as As fragment, cationic species as Ge fragment **D**).

	$(SiH_3)_2GeAsPh$	$(OCH_3)_2GeAsOCH_3$	$(CH_3)_2GeAsCH_3$	H_2GeAsH	$(OH)_2GeAsOH$	$(NH_2)_2GeAsNH_2$	F_2GeAsF	$Cl_2GeAsCl$	$Br_2GeAsBr$	$(OH)_2GeAsCN$	$(OH)_2GeAsBr$	$(CH_3)_2GeAsBr$	$(CH_3)_2GeAsCN$
C[d]													
[a]ΔE^{int}	-232.77	-232.78	-274.90	-287.47	-243.59	-256.18	-240.55	-230.60	-223.18	-280.64	-256.36	-278.03	-307.82
[a]ΔE^{Pauli}	309.44	223.28	412.09	378.53	198.27	253.98	234.87	199.97	196.22	210.73	290.14	333.49	396.39
[a]ΔE^{elst}	-254.68	-207.50	-313.42	-301.84	-198.86	-234.76	-202.38	-186.88	-178.97	-211.28	-234.95	-289.96	-315.52
[a]ΔE^{orb}_{tot}	-277.04	-243.21	-368.43	-361.35	-239.40	-270.68	-270.16	-238.32	-234.00	-275.71	-306.58	-315.93	-383.21
[a]ΔE^{disp}	-10.48	-5.35	-5.13	-2.81	-3.59	-4.72	-2.89	-5.37	-6.42	-4.39	-4.97	-5.63	-5.48
D[d]													
[a]ΔE^{int}	-240.57	-236.06	-242.76	-268.98	-256.05	-225.32	-273.82	-242.69	-231.15	-223.26	-238.70	-224.43	-212.47
[a]ΔE^{Pauli}	335.03	351.28	359.5	413.51	361.13	317.10	314.56	279.20	286.01	336.84	293.83	-224.43	389.12
[a]ΔE^{elst}	-233.87	-276.88	-244.7	-314.3	-299.77	-238.06	-267.67	-214.65	-219.88	-260.25	-221.78	-303.09	-277.35
[a]ΔE^{orb}_{tot}	-331.26	-305.12	-352.43	-365.38	-313.82	-299.64	-317.83	-301.92	-290.86	-295.46	-305.79	-335.30	-318.76
[a]ΔE^{disp}	-10.48	-5.35	-5.13	-2.81	-3.59	-4.72	-2.89	-5.37	-6.42	-4.39	-4.97	-5.63	-5.48

[a] All values are reported in kcal·mol^{-1};